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Guidelines for Phase Separations in High-Temperature and Supercritical Water Solutions:

A Report on a Workshop Organized by the U.S.
Army Research Office and the Forschungszentrum
Karlsruhe, 7-9 July 1999

Robert W. Shaw and Nikolaos Boukis (editors)

ARL-SR-99

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Army Research Laboratory

Research Triangle Park, NC 27709

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Sponsored by

U.S. Army Research Office

Research Triangle Park, NC 27709

Army European Research Office

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Abstract

The U.S. Army is developing supercritical water oxidation for destruction of military toxic materials. The properties of high-temperature aqueous solutions are not, in most cases, well known. Understanding the phase behavior of these solutions will facilitate design and efficient operation of high-temperature water reactors. A U.S. Army workshop held at the Forschungszentrum Karlsruhe in July 1999 assembled experts on phase behavior to develop guidelines that, in the absence of more complete knowledge of solution properties, will aid reactor designers and operators. The experts presented papers on model systems, properties of high-temperature aqueous solutions, and chemistry in high-temperature water. Following these presentations, the experts developed some of the desired rules of thumb and made recommendations for research to develop these guidelines further. This workshop report includes the presentation papers, guidelines, and recommendations for research.

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1. Introduction

Supercritical water (SCW) oxidation (SCWO) provides a powerful means to transform toxic organic materials into simple, relatively inert oxides. Water at high temperatures and pressures is an active medium, however, and its properties and those of its solutions are only partially understood. Indeed, two principal challenges to broad use of this technology are (1) the materials requirements for the reactor and the heatup and cooldown sections, and (2) the incomplete understanding of and ability to predict the phase behavior of SCW solutions.

Phase separations have the potential to impair the operation of an SCWO reactor (1) by dramatically changing transport properties (especially in the presence of dynamically separating liquid and solid phases), (2) by generating solid particles that may plug reactor orifices and deposit on reactor surfaces, and (3) by producing a highly corrosive electrochemical environment.

1.1 Objectives for This Workshop

We sought to develop (or recommend methodologies to develop) guidelines/rules of thumb for phase separations in organic/salt/gas/aqueous solutions in SCWO processing for defined sets of feed compositions. Useful speculations about these phase separations are in the areas not only of equilibrium thermodynamics (e.g., solubility), but also of the kinetics of phase separation and growth (e.g., the problem of heterogeneous nucleation). The phase separation guidelines are intended to indicate regions of safe (predictable) reactor operation.

This workshop sought to develop either the rules themselves or a specific plan for developing them, and we seek to give these rules as wide a distribution as possible. We planned the workshop agenda to provide important background information from experts on phase behavior, chemical reactions, and reactor engineering in high-temperature water.

1.2 Participants

We chose as participants a range of experts on phase equilibria, on properties of high-temperature water and its solutions, and on chemical reactions in high-temperature water. Invited talks by the participants provided the basis for subsequent discussions. The participants divided into two focus groups (Alpha and Omega) and developed answers to the workshop questions and recommendations for future research.

Participants are shown in figure 1. Contact information is provided below the figure.



Figure 1. Participants in the workshop. Left to right: Boukis, Tester, Sengers, Shaw, Simonson, Franck, Ederer, Anderko, Abeln, Weingärtner, Schmieder, Peters, and Hong.

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*Steven Buelow, Los Alamos National Laboratory, contributed to the planning of this workshop, especially in the development of model systems. He was unable to attend.

1.3 Specific Questions

The workshop sought to answer the following specific questions.

What are the temperature, pressure, density, composition (T, P, ρ, x) regions where equilibrium conditions are such that liquid phase separation (including brines) will not occur?

What are the T, P, ρ, x regions where equilibrium conditions are such that solid phase separation will not occur?

What is the extent of pyrolysis (hydrolysis of feed as materials are brought up to temperature) in the heatup section of a reactor? How will these reactions influence phase separation?

How will the kinetics (including homo- and heterogeneous nucleation and growth) of phase separation affect the relative time scales of kinetic processes and reactor residence? To what extent does supersaturation occur?

How sensitive are equilibrium and kinetic phenomena to changes in cation and anion composition?

1.4 Model Systems

The workshop also sought to determine what feed materials should be considered.

Some of the participants (S. Buelow, G. Hong, R. Shaw, J. Tester) met before the workshop to develop a list of model systems for study at the workshop. They discussed several approaches to developing the list (including classifying by real materials of interest and abstracting the classification of feed materials) and decided to develop a list of real materials (see presentation by Hong, p 9).

1.5 Report of This Workshop

This report comprises the presentations by the participants and the reports of the focus groups. The summary of recommendations that follows is a concise statement of the conclusions of the focus groups and their recommendations for research; this statement is the principal outcome of the workshop. The presentation papers and group reports provide backup material on which the summary is based. The presentation papers also provide a unique guide to current understanding of phase behavior in high-temperature aqueous solutions.

1.6 Acknowledgements

We thank the U.S. Army Research Office, U.S. Army European Research Office, U.S. Army Assembled Chemical Weapons Assessment Program, and the Forschungszentrum Karlsruhe for support. We thank the Forschungszentrum for the use of their excellent facilities, made available by Prof. Dr. E. Dinjus, Director of the Institute for Technical Chemistry, and we thank Prof. Gerhard Schneider for encouragement.

2. Summary of Recommendations

This section briefly summarizes the discussions and conclusions of the two focus groups. More information and justification are given in the Reports of the Focus Groups (sect. 6), although even those reports are brief and incomplete. This brevity is inevitable, given the ambitious scope of the workshop, which sought to cover a number of complex topics in a limited time. Invited presentations on these topics (sect. 3 to 5) provided the background and basis for the focus group discussions.

Although the following recommendations are based on expert evaluations, the database is very incomplete, and the experience available for SCWO (a relatively new technology) is limited. The focus groups did include some of the world's experts, however, and we believe that their inferences and suggestions are valuable. The active presence of a range of experts and the novelty of this activity encouraged us to make the outcome available to others. Nevertheless, we warn those who are developing SCWO technology to proceed with caution.

2.1 Phase Behavior Rules of Thumb

Rule of Thumb 1

All gases/organics will be completely miscible with water (or destroyed) above 400 °C and at pressures from 100 bar to at least 1 kbar.

Rule of Thumb 2

Type 1 salts (for which the solid does not intersect the vapor–liquid critical line) will show vapor–liquid phase separation beginning in a region that is roughly the extension of the vapor pressure of pure water in the P – T phase diagram.

Rule of Thumb 3

Franck hypothesis: Above 400 °C, and at densities below 0.5 kg dm⁻³, no divalent ions exist. They are partially or fully associated.

Rule of Thumb 4

For Type 2 salts (for which the solid interrupts the vapor–liquid critical line), the solubility decreases with temperature (the temperature–liquid composition three-phase curve moves to lower compositions at increasing temperature). Salts in this class have at least one divalent ion, but a salt with one divalent ion is not necessarily Type 2. Type 2 salts will always produce solids under SCW conditions.

Rule of Thumb 5

Binary fluid phase diagrams of interest to SCWO applications are mostly Type I (continuous critical line) and Type III (critical line interrupted by liquid-liquid-vapor three-phase line).

Rule of Thumb 6

Knowledge of the initial slopes of the critical line in P - T , P - x , and T - x space yields the useful Krichevskii parameter, which characterizes solute-mixture behavior near the solvent critical point.

2.2 Research Needed to Characterize Phase Behavior

The following are areas of research that are required for further understanding of phase behavior:

1. Nucleation, including rates. Phase boundaries for the solid. Behavior during superheating.
2. Transport properties for the calculation of design parameters such as heat transfer coefficients.
3. Experimental determination of the properties of model ternary systems.
4. Development of equations of state for systems containing salts, water, and gases.
5. Determination of the static dielectric constant and viscosity (for estimation of diffusion coefficients) of homogeneous water-nonpolar mixtures at all compositions. Both experimental and theoretical/computational research is needed. The first systems studied should be water-carbon dioxide, water-methane, and water-hexane up to 500 °C and 300 MPa. Ternary systems should also be studied.

2.3 Recommendations for Operating an SCWO Process for Waste Destruction

1. Operate at low feed concentrations to avoid undesired reactions in the heatup stage. Bad reactions include self-oxidation leading to uncontrollable thermal runaway and generation of highly corrosive reaction products; one may also avoid plugging by solid precipitates.
2. Cold injection of the feed will help avoid reactions occurring outside the reactor in the heatup sections.
3. Pure oxygen injected directly into the reactor will reduce both gas volumes in solution and salt precipitation; compressed oxygen, however, is potentially dangerous.
4. Quench to 250 °C immediately after the process stream has left the reactor to redissolve salts.

5. Neutralize the acidic product stream with KOH rather than with NaOH. KCl is more soluble (but also more corrosive) than NaCl. (Not all participants support this argument.)

2.4 Recommendations for Specific Wastes

Table 1 of Hong's presentation on model systems (p 11) sorts the wastes of interest into four categories.

1. Explosives and propellants: Hydrolyze the feed at low pressure and below 100 °C. Avoid excess of NaOH. Operate in a highly diluted regime to avoid thermal runaways.
2. Halogenated organics: For category B1, avoid surfactants containing S and P and the formation of phosphates and sulfates. Use KOH to neutralize. Defoaming agents may be necessary. Category B2 and B3 wastes should be processed very dilute. Pre-neutralize with NaOH or KOH and inject cold into the reactor.
3. Chemical weapons: Hydrolyze first; KOH may be preferable to NaOH. Precipitation of phosphates is likely to occur. Process very dilute to keep the particle density low. Cold injection of the hydrolyzed feed is not necessary.
4. Organic wastes: Cold inject the feed into the reactor. Neutralize with KOH. Quench downstream to redissolve salts. Category D3 contains inorganic material; very little information exists from which to infer recommendations.

3. Invited Talks 1: Model Systems

Presentations in this section introduced the waste materials of interest. Hong and Peters discussed the compositions of candidate materials for supercritical water oxidation. They focused on military toxic materials: explosives, propellants, and chemical weapons. They also discussed halogenated and other organic compounds that present a disposal problem to the military, as well as to civilian industry. Nearly all these materials will react to produce ionic solutions, some of them corrosive. Hong gave details of model system compositions and discussed relevant studies of solubility and phase behavior from the literature. Peters briefly discussed the likely behavior of feed materials of interest. Subsequent discussions of guidelines and research recommendations appearing in this report were based on these model systems.

Model Systems and System Classification for Phase Separations in SCWO

Glenn T. Hong
General Atomics

Background

The process of supercritical water oxidation (SCWO) operates at pressures in the range of 250 bar and 600 °C. Inherent in the process are a number of possible high-pressure phase separations that are of key importance in determining the overall system design, as well as the design of individual components such as the reactor. As the potential phase separations vary considerably with the stage of the process, it is convenient to divide the process into three zones of phase behavior. The first zone for which phase separations are considered is the heatup zone, in which pressurized process fluid is typically passed through a heater or heat exchanger and raised to a temperature in the range of the critical temperature of water, i.e., 374 °C. A key phase-separation problem that may arise in this zone is the immiscibility of gaseous oxidant and organic with water, with a resultant potential for uncontrolled reaction in the preheater. In extreme cases, this may lead to pipe wall overheating and rupture. With pure oxygen as the oxidant, metal burning is an added danger.

Within the heatup zone, inorganic solids may exhibit decreasing solubility with increasing temperature. Such retrograde solubility is exhibited by many common salts, such as sodium sulfate and sodium carbonate, and can lead to scaling of heat-transfer surfaces or plugging. Likewise, in the absence of oxidant, certain organic materials are prone to polymerization to form insoluble char or tar, which may also lead to scaling of heat-transfer surfaces or plugging. During preheating, other organic materials may be hydrolyzed to release heteroatoms that form corrosive species; e.g., many chlorinated hydrocarbons will form hydrochloric acid, although this problem does not concern phase separation. For all the preceding reasons, the order and temperature/pressure conditions under which the various input streams are introduced into the SCWO system are of great importance. For feed materials with sufficient heating value, the best option is frequently avoidance of a discrete heatup zone by direct injection of unheated feed material into the reactor.

The second zone for phase separations is the reaction zone, in which temperatures in the range from 375 °C to 650 °C are encountered. In this zone gases become completely miscible with the bulk supercritical water phase. Organic materials rapidly oxidize to inorganic species, primarily carbon dioxide and water, which are also miscible with the bulk fluid phase. Certain organic feed materials may also form acids such as HCl or H₂SO₄. If unneutralized, these will be miscible with the bulk fluid phase or form a

second fluid phase. In either case corrosivity is a concern, but phase separation (if any) should not pose additional difficulties. The primary concern in terms of phase separation is the precipitation of salts as solid particles or brine droplets. Solid precipitates are frequently sticky and may bring about plugging of the reactor. Brine phases on the other hand should not plug the reactor, but are dense ionic fluids with potential high corrosivity.

The third zone for phase separations is the cooldown zone, in which process stream temperatures are reduced to below 375 °C before discharge. As subcritical temperatures are achieved, most salts will redissolve, but gas phase immiscibility will again arise.

Of the various phase separations that may occur during the SCWO process, those involving salt precipitation most frequently drive the process and reactor design. For this reason, it is the equilibrium phase behavior of salt-water systems that is the focus of this presentation.

Model Salt–Water Systems and Classification

Model salt–water systems for SCWO should be important systems that carry a reasonable chance of SCWO implementation. *Importance* may be defined in a number of ways (for example, economic or political importance), and the term does not necessarily imply large throughput. An extreme example would be certain applications of SCWO investigated for use in the U.S. space program, where throughputs in the range of only 100 g/min are of interest.

Model systems may also be systems that mimic the behavior of important systems. This definition is useful for the current state of the art, where experimental data are frequently very limited or nonexistent. For the purposes of this presentation, it is assumed that the behavior of salt–water systems is modeled by the behavior of the dominant salts: i.e., that the minor constituents that may be present will have only a slight effect. Operationally, it may be found that this assumption is problematic, especially during the course of extended system operation. For example, it may be found that slow deposition of a minor salt constituent can greatly affect system operation. Such is the case with the related process of wet oxidation, where regular shutdown of the plant is required for removal of scaling due to calcium salts.

In the United States, the most important current applications are in the defense industry. Table 1 provides a synopsis of many of the feed materials of interest. The most important salts are chloride, sulfate, carbonate, phosphate, and fluoride, typically with a sodium cation. These salts and their mixtures form a baseline set of model systems. This set also happens to include the salts that are most frequently encountered in industry—chloride, sulfate, and carbonate with a sodium cation.

Experimental work on the phase behavior of salt–water systems has primarily been carried out by the geochemical community, with the majority of contributions coming from the United States or the former Soviet Union.

Table 1. U.S. DOD compositions of interest.

Original system	Products
A. Explosives and propellants	
A1. RDX (80 ppm) and TNT (20 ppm) contaminated water	Gases and liquids only
A2. Base hydrolyzed energetics, e.g., 17% TNT+RDX in 10% NaOH	NaHCO ₃ (in effluent) or Na ₂ CO ₃ (in reactor)
B. Halogenated organics	
B1. 20–80 ppm PCB with 2% surfactant contaminated water	If neutralized with Na and surfactant contains S, a mixture of NaCl and Na ₂ SO ₄ will result. With excess sodium, NaHCO ₃ (in effluent) or Na ₂ CO ₃ (in reactor) will also be present.
B2. 1,1,1 trichloroethane	If neutralized with Na, NaCl will result. With excess sodium, NaHCO ₃ (in effluent) or Na ₂ CO ₃ (in reactor) will also be present.
B3. Polychlorotrifluoroethylene lubricating oil	If neutralized with Na, a mixture of NaCl and NaF will result. With excess sodium, NaHCO ₃ (in effluent) or Na ₂ CO ₃ (in reactor) will also be present.
C. Chemical weapons	
C1. VX hydrolysate: 15% ethyl methylphosphonic acid, 1.3% methylphosphonic acid, 16% diisopropylaminoethanethiol, 1.3% bis (diisopropylaminoethyl) disulfide. 14% total organic carbon, 3.8% total S, 3.8% total P, 8.8% total Na	A 1:1 molar mixture of NaH ₂ PO ₄ and Na ₂ SO ₄ will result in the liquid effluent. With excess sodium, Na ₂ HPO ₄ will also be present.
C2. GB hydrolysate: 5–6% isopropyl methylphosphonic acid, 5–6% NaF, NaOH	A 1:1 molar mixture of NaH ₂ PO ₄ and NaF will result in the liquid effluent. With excess sodium, Na ₂ HPO ₄ will also be present.
C3. HD hydrolysate: 2.7% thiodiglycol, NaCl, NaOH	A 2:1 molar mixture of NaCl and Na ₂ SO ₄ will result. With excess sodium, NaHCO ₃ (in effluent) or Na ₂ CO ₃ (in reactor) will also be present.
D. Organic wastes	
D1. Photographic waste solution (simulated): 11% ammonium sulfate, 2% Na sulfite, 1% K sulfite, 0.4% acetic acid, 0.5% pentanol	If neutralized with Na or K, a mixture of Na ₂ SO ₄ and K ₂ SO ₄ will result. With excess sodium, NaHCO ₃ (in effluent) or Na ₂ CO ₃ (in reactor) will also be present.
D2. Coolant: ethylene glycol	Gases and liquids only
D3. Lubricating oil: 40–70% phenylmethylsiloxane, 60–30% molybdenum disulfide	Siloxane should form silica. MoS ₂ products are unknown but possibly molybdenum oxide and sulfuric acid.
D4. Hydraulic fluid: Mixture of glycol and glycol ether	Gases and liquids only

Prepared by Glenn Hong, Jefferson Tester, Steve Buelow, and Robert Shaw (original systems provided by Shaw).

Fortunately, there is a large overlap of systems of geochemical importance with those of interest to SCWO. Classification of salt–water systems at SCWO conditions has primarily been carried out by Russian investigators at the Kurnakov Institute in Moscow; these systems include many binary and a few ternary systems, as described below.

Binary Salt–Water Systems

Salt–H₂O binary systems are classified as one of two types, depending on whether critical behavior is observed in saturated solutions (i.e., in the presence of a solid phase). Type 1 systems do not exhibit critical behavior in saturated solutions and therefore have a continuous solidus (solid–liquid–vapor or *S–L–V* equilibrium line) running from the eutectic point of the mixture to the triple point of the salt. Such systems exhibit high solubility near water’s critical temperature. Type 1a, the most common, has a continuous critical locus extending from the critical point of water to the critical point of the salt, although because of the extreme temperature the latter has usually not been measured. The classic example of a Type 1a system is NaCl–H₂O, which conforms to the pressure–temperature–composition (*P–T–x*) diagram shown in figure 1a. While the critical line is not interrupted by precipitation of a solid phase in Type 1 systems, it may be interrupted by formation of a second liquid phase. This type of behavior is designated Type 1b and is shown in the *P–T–x* diagram of figure 1b.

A question of interest to the present workshop is in what regions liquid and solid phases may be present for the various salt–water systems. A partial answer to this question may be gleaned from the *P–T* projection of the solidus in conjunction with *T–x* (or *P–x*) sections. Figure 2 shows the NaCl *T–x* section at 250 bar (Hong et al, 1995). This *T–x* section shows two lines of *S–*

Figure 1. *P–T–x* diagram for (a) Type 1a systems and (b) Type 1b systems, (from Valyashko, 1977).

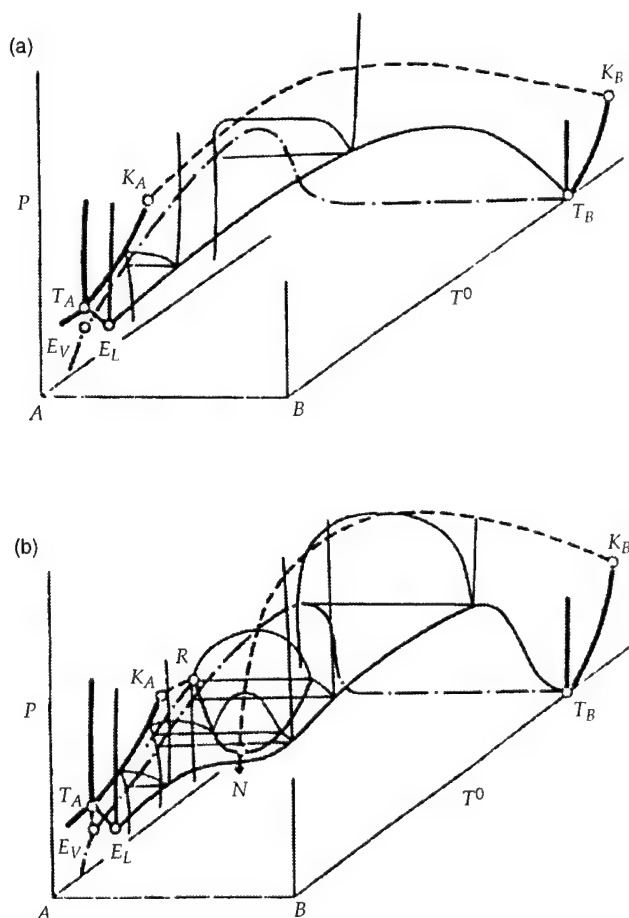
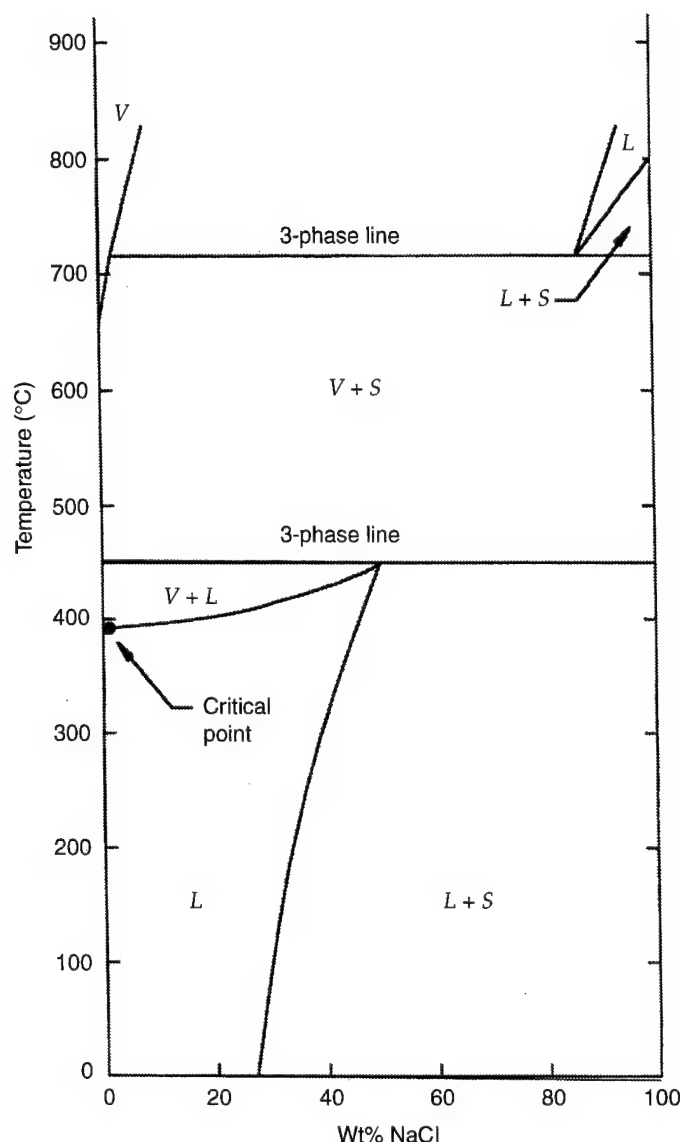


Figure 2. T - x diagram for NaCl-H₂O at 250 bar (from Hong et al, 1995).



L - V equilibrium, corresponding to the two points of the solidus at 250 bar shown in figure 3. Between the two S - L - V lines, or in other words at points falling within the solidus of figure 3, no liquid phase appears.

Type 2 systems exhibit critical behavior in saturated solutions and therefore have a discontinuous solidus. The low-temperature portion of the solidus has a terminus at the eutectic point of the mixture, while the high-temperature portion of the solidus has a terminus at the triple point of the salt. Such systems exhibit very low solubility, typically in the range of parts per million, near water's critical temperature. As with Type 1 systems, the critical line may or may not be interrupted by formation of a second (in this case metastable) liquid phase. Type 2a behavior is shown in the P - T - x diagram of figure 4a, while Type 2b behavior is shown in figure 4b. Well-known examples of Type 2b systems include Na₂SO₄-H₂O and Na₂CO₃-H₂O. Similarly to Type 1 systems, in Type 2b systems no liquid phase may appear at P - T coordinates below the solidus or in the gap between the critical end points. The latter are designated P and Q in figure 4.

Figure 3. P - T projection of solidus for $\text{NaCl-H}_2\text{O}$ (from Sourirajan and Kennedy).

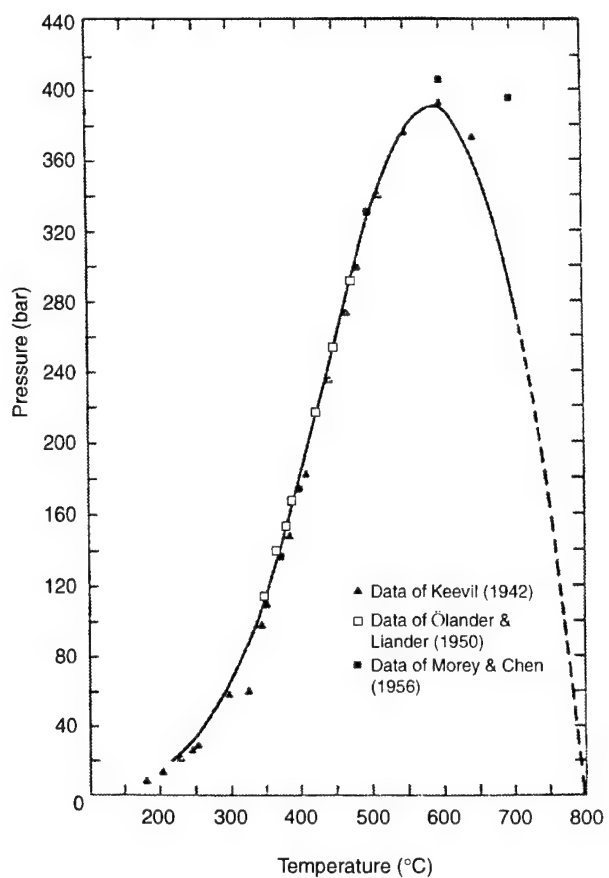
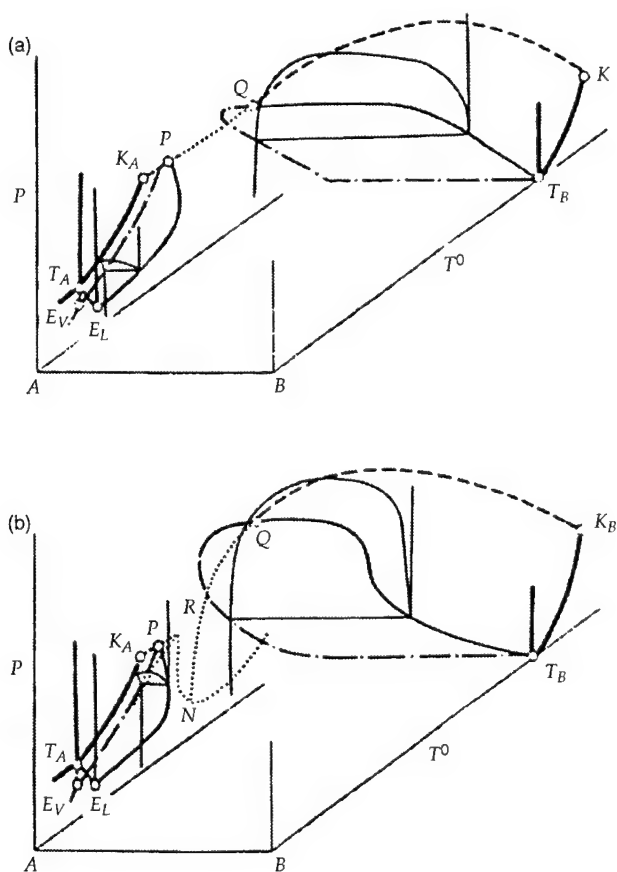


Figure 4. P - T - x diagrams for (a) Type 2a systems, and (b) Type 2b systems (from Valyashko, 1977).



Marshall (1975) has presented a summary diagram of solubility for a number of salts. Based on the solubility in the range of water's critical temperature, the systems may be classified as Type 1 or Type 2, as presented in table 2.

Valyashko (1976, [1999*]) has classified a number of salt-water systems in a manner that shows trends in the behavior. This classification is reproduced in table 3. Solubility increases for a given anion with a larger cation, and likewise for a given cation with a larger anion. Thus, the larger ions correlate with a shift in behavior from Type 2 to Type 1.

Type 1 and Type 2 solubility behavior may also be roughly correlated with melting temperature, although there is considerable overlap. Type 1 salts possess melting temperatures below 800 to 1000 °C, while Type 2 salts possess melting temperatures above 700 to 800 °C.

Table 2. Classification of salt-water systems by solubility behavior (interpretation of Marshall, 1975).

Type 1 salts	Type 2 salts
LiClO ₄	Li ₂ SO ₄
NaCl, NaBr, NaI, NaNO ₃ , Na ₂ SeO ₄	Na ₂ SO ₄ , Na ₂ CO ₃ , Na ₃ PO ₄
KCl, KBr, KI, KNO ₃ , KBrO ₃ , KIO ₃ , K ₂ CrO ₄ , KReO ₄	K ₂ SO
NH ₄ Cl, NH ₄ Br, (NH ₄) ₂ SO ₄	
MgCl ₂ , MgI ₂	
CaCl ₂	
SrCl ₂ , SrBr ₂ , Sr(NO ₃) ₂	
BaCl ₂ , BaBr ₂ , Ba(NO ₃) ₂	
MnCl ₂	
FeCl ₃	
ZnCl ₂	
CdCl ₂ , CdBr ₂ , CdI ₂ , Cd(ClO ₄) ₂	
HgCl ₂	
TlCl, Tl ₂ SO ₄	
PbCl ₂ , PbBr ₂	

Table 3. Classification of salt-water binary systems (Valyashko, 1976).

Type 2 salts	Type 1 salts
LiF, NaF	KF, RbF, CsF
LiF	LiCl, LiBr, LiI
NaF	NaCl, NaBr, NaI
Li ₂ CO ₃ , Na ₂ CO ₃	K ₂ CO ₃ , Rb ₂ CO ₃
Li ₂ SO ₄ , Na ₂ SO ₄ , K ₂ SO ₄	Rb ₂ SO ₄
Na ₂ SO ₄	Na ₂ SeO ₄
Li ₂ SiO ₃ , Na ₂ SiO ₃	K ₂ SiO ₃
Li ₃ PO ₄ (?), Na ₃ PO ₄	K ₃ PO ₄
CaF ₂	CaCl ₂ , CaBr ₂ , CaI ₂
SrF ₂	SrCl ₂ , SrBr ₂
BaF ₂	BaCl ₂ , BaBr ₂

* Reference to Valyashko (1999) added in proof.

Ternary Salt–Salt–Water Systems

Valyashko (1971) has classified ternary salt–salt–water systems according to the behavior of the bounding binary salt–water systems. For a Type 1 Subtype A ternary, both constituent binaries are of Type 1, while for a Type 1 Subtype B ternary, both constituent binaries are of Type 2. The Type 1 Subtype C ternary corresponds to the mixed case, in which one constituent binary system is of Type 1 and the other is of Type 2. T - x projections for these systems are shown in figure 5. In these diagrams the right-hand face of the triangular prism gives the behavior of the binary salt mixture. The other two faces depict the behavior of the constituent binary salt–water systems. The eutonic curves are shown as the light, continuous curves starting at the eutectic of the dry salt mixture (right-hand prism face) and extending toward the water apex.

For ternary systems, the analog to the binary solidus is the eutonic curve, which represents four-phase equilibrium among two solid phases, saturated liquid, and vapor. The eutonic curve has its high-temperature terminus at the normal eutectic point of the salt mixture. Figure 6 shows the P - T projection of the eutonic curve (labeled "7") for the system NaCl - Na_2SO_4 - H_2O , terminating at the eutectic temperature of 628 °C. In a manner analogous to the binary solidus, no liquid phase appears at conditions falling within the eutonic curve. This is more clearly illustrated in figure 7, which shows a series of T - x diagrams for this system at 225 bar. As seen in figure 6, the eutonic curve intersects 225 bar at two points. Figure 7 includes the T - x diagrams at these points, 473 °C and 516 °C. Between these temperatures (e.g., at 500 °C), liquid phase is absent.

It is to be noted that although the Na_2SO_4 - H_2O system is of Type 2 and has an interrupted solidus, the mixture with the Type 1 salt NaCl has a

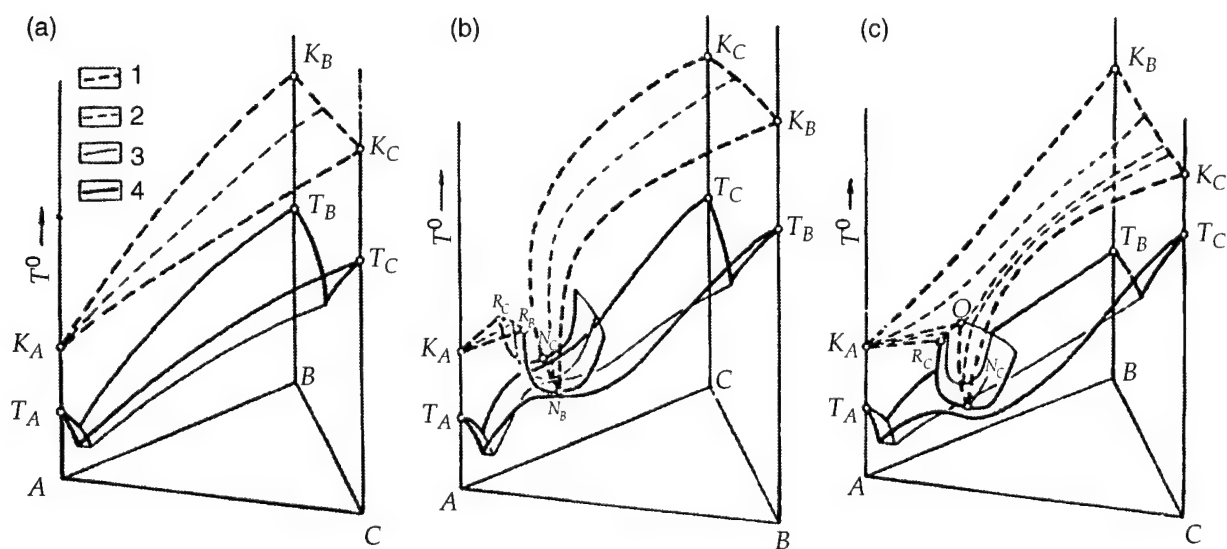


Figure 5. T - x projection of phase diagram for ternary systems of Type 1: (a) subtype A, (b) subtype B, and (c) subtype C (from Valyashko, 1971).

Figure 6. P - T projection of eutonic curve for NaCl- Na_2SO_4 - H_2O system (from Ravich et al, 1951). CP = critical point of water.

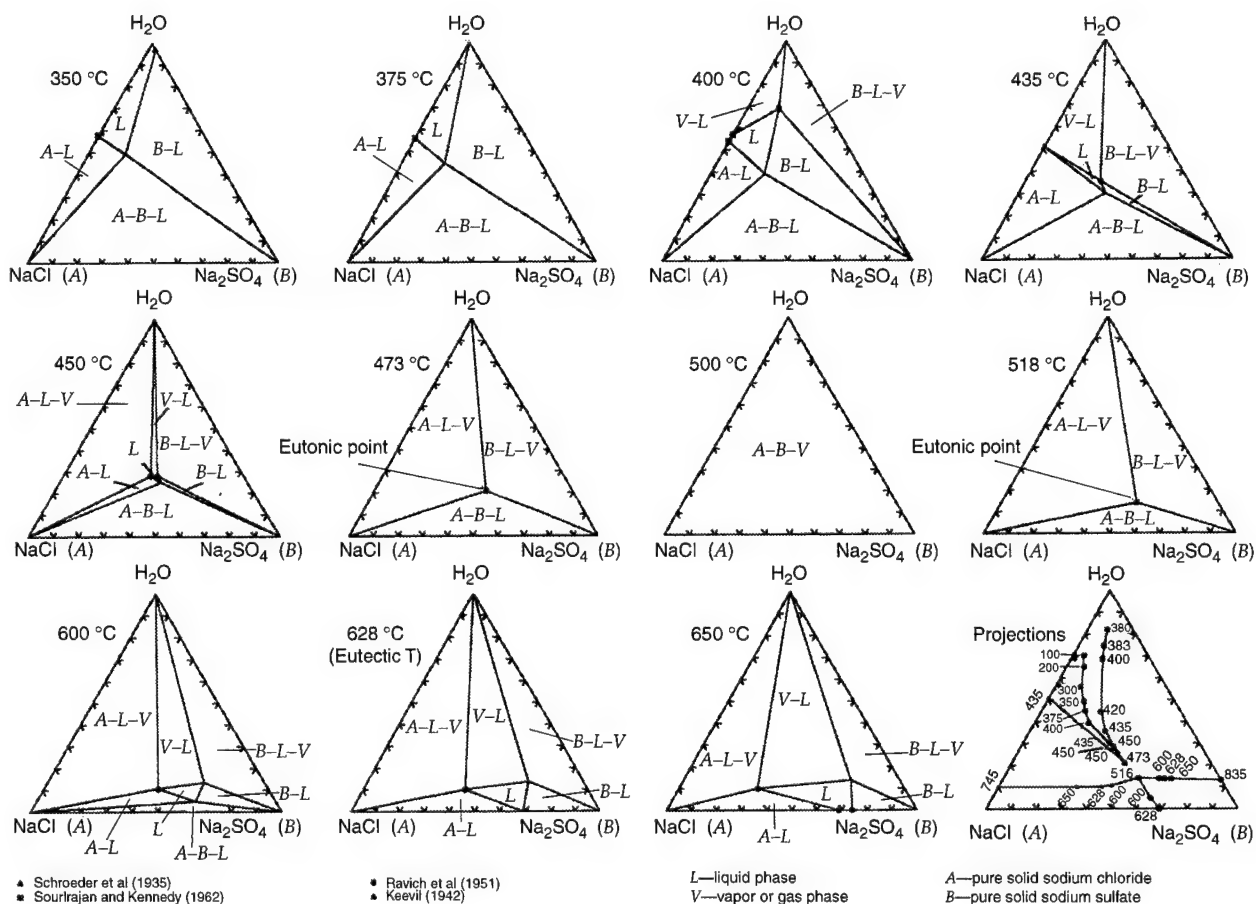
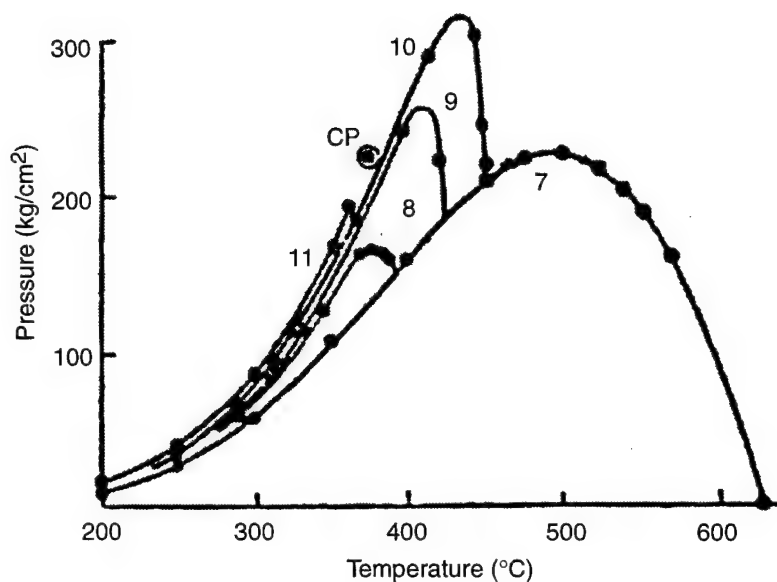


Figure 7. Temperature progression of phase diagrams at 225 bar for NaCl- Na_2SO_4 - H_2O system. Very small vapor region near H_2O apex has not been shown. Numbers on projection refer to temperature in $^{\circ}\text{C}$ (from Hong et al, 1995).

continuous eutonic curve. As shown in figure 5b, a continuous eutonic curve may be observed even when both constituent salt–water binary systems are of Type 2. An example of such a system is $\text{K}_2\text{SO}_4\text{--KLiSO}_4\text{--H}_2\text{O}$ (Ravich, 1970).

Quaternary and Higher Systems

Classification of salt–water systems has not been carried out beyond ternary systems. The usefulness of or need for further classification is unclear. The large number of permutations will generally require end users of the technology to develop their own phase behavior data. Also, at this level of detail, the required information will frequently be restricted to a fairly localized composition range. Minor constituents may also play an important role in these circumstances.

Consideration of noncondensable gases in binary and ternary salt–water systems is a necessary exercise, in that oxidant, carbon dioxide reaction product, and possibly inert gases such as nitrogen will be present in SCWO systems. Perhaps the most relevant data in the literature are for the system $\text{NaCl--CO}_2\text{--H}_2\text{O}$ (Takenouchi and Kennedy, 1965; Gehrig et al, 1986). In the absence of experimental data, use of the salt–water or salt–salt–water phase diagrams at the system water partial pressure should provide a reasonable first approximation. When separate gas and liquid phases are present (and perhaps even if they are not), mutual attraction between salt and water probably makes this approximation a bit exaggerated; i.e., the salt–water or salt–salt–water phase diagrams at somewhat greater than the system water partial pressure would be more accurate.

Conclusions

Model systems for phase separations in SCWO should include the salt anions chloride, sulfate, carbonate, phosphate, and fluoride, typically with a sodium cation. A classification scheme for binary salt–water and ternary salt–salt–water systems already exists, although detailed solubility information is usually unavailable. Phase behavior and solubility information for systems containing carbonate, phosphate, and fluoride sodium salts is scarce, and studies of these systems would be of particular value. Investigation of some salt–water systems containing O_2 , N_2 , and/or CO_2 would also be of particular value.

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Characterization of the Feed and Products: Brief Comments

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The Feed

Material

Explosives and propellants
Halogenated organics
Chemical weapons
Organic wastes
Conclusion: Feed contains organic and inorganic (salts) material.

Phases

Various solid phases
Most likely more than one liquid phase
A gaseous phase
Preheating and pressurizing will reduce the number of phases; solids, however, may remain present.

The Products

Composition

The SCWO reaction reduces the complexity of the original mixture.

Phases (at reactor conditions)

Various solid phases
Most likely one liquid phase

Phases (after cooling down)

Various solid phases
One liquid phase
A gaseous phase

Observations

It makes no sense to try to describe the feed thermodynamically because—

- The feed stream does not cause real operational difficulties.
- The mixture is too complex.

- There is no relationship between the thermodynamics of the feed and that of the product stream.

Most important is the availability of an *elemental analysis* of the feed, because it defines the nature of the product stream.

There is a serious lack of experimental information on systems of the nature water + salt(s) + gas (CO_2 , N_2 , O_2 , ...), ranging from reactor conditions to ambient.

Thermodynamic modeling of the phase behavior of the product stream at reactor conditions, in principle, seems to be feasible.

At lower temperatures, the modeling of the product stream is problematic.

More insight is needed in the formation/decomposition of ion pairs as a function of process conditions (P , T).

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4. Invited Talks 2: Properties of Solutions in High-Temperature Water

The presentations in this section provided information on scientific issues underlying treatment of wastes in high-temperature water. Anderko, Simonsen, Sengers, and Weingaertner presented current knowledge of the behavior of aqueous salt solutions at high temperatures. Anderko described modeling and equations of state and showed that considerable progress has been made in characterizing high-temperature aqueous solutions over a wide range of temperatures, pressures, and compositions. Weingaertner summarized current knowledge of dielectric constants of aqueous solutions and presented some recent measurements. Simonsen discussed models for reaction, solution thermodynamics, and equilibria in high-temperature water. He showed that an extensive data base at lower temperatures and new approaches (including new equations of state) hold promise for significant advances in predictive capability for solution properties and reaction behavior. Sengers presented new information about salt solutions highly relevant to the behavior of chemical weapon agents in water: sodium sulfate and sodium carbonate.

Modeling Salt Solutions in High-Temperature and Supercritical Water

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OLI Systems, Inc.

The objective of this review is to summarize the state of the art in modeling high-temperature salt + water systems. Since excess Gibbs energy models are not practical at near-critical and supercritical conditions, the key to successful modeling of such systems is the development of accurate equations of state. It has been recognized that the development of equations of state for salt solutions is more complex than for nonelectrolyte systems. The phase behavior of salt-containing systems is very different from that of nonelectrolyte systems. For example, the critical line for NaCl+H₂O is not interrupted by liquid phase splitting, in contrast to the lines for nonelectrolyte systems with strongly dissimilar critical temperatures. Also, the concentrations of salts in the vapor phase vary by many orders of magnitude, which puts stringent requirements on the equation of state.

Development of a Comprehensive Equation of State for Selected Salt Systems

A successful equation of state must recognize the most important intermolecular interactions in the system. For salt solutions, the interactions among ions, ion pairs, and solvent molecules need to be considered. However, to make the model tractable, it is necessary to introduce a reference system that approximates the behavior of the real system and makes it possible to obtain closed-form expressions for thermodynamic functions. At low and moderate temperatures, the universally accepted reference system invokes the idea of ions interacting in a dielectric continuum. Such a reference system becomes impractical at high temperatures because of the prevalence of ion pairs. Therefore, Anderko and Pitzer (1993a) proposed a different reference system, in which ion pairs and solvent molecules are treated as hard-sphere dipolar entities. Analytical expressions for such a reference system are available from perturbation theory. Thus, we can define the equation of state by writing the residual Helmholtz energy as

$$a = a^{rep} + a^{dip} + a^{pert},$$

where the superscripts *rep*, *dip*, and *pert* refer to the repulsive, dipolar, and perturbation contributions, respectively. The perturbation contribution represents the deviations between the reference system and real fluids and is expressed by an extended van der Waals form. This formulation makes it possible to reproduce phase equilibria and volumetric properties for the NaCl+H₂O and KCl+H₂O systems with very good accuracy. Figures 1 to 3 show sample results for NaCl+H₂O. The model can also reproduce the phase behavior of water + nonelectrolyte systems. This is illustrated in figure 4 for the O₂+H₂O system. Thus, it has been demonstrated that the equation of state based on the dipolar, ion-paired reference system is appropriate for modeling the phase behavior of SCWO systems.

Figure 1. Compositions of coexisting vapor and liquid phases in NaCl+H₂O systems calculated from equation of state of Anderko and Pitzer (1993a).

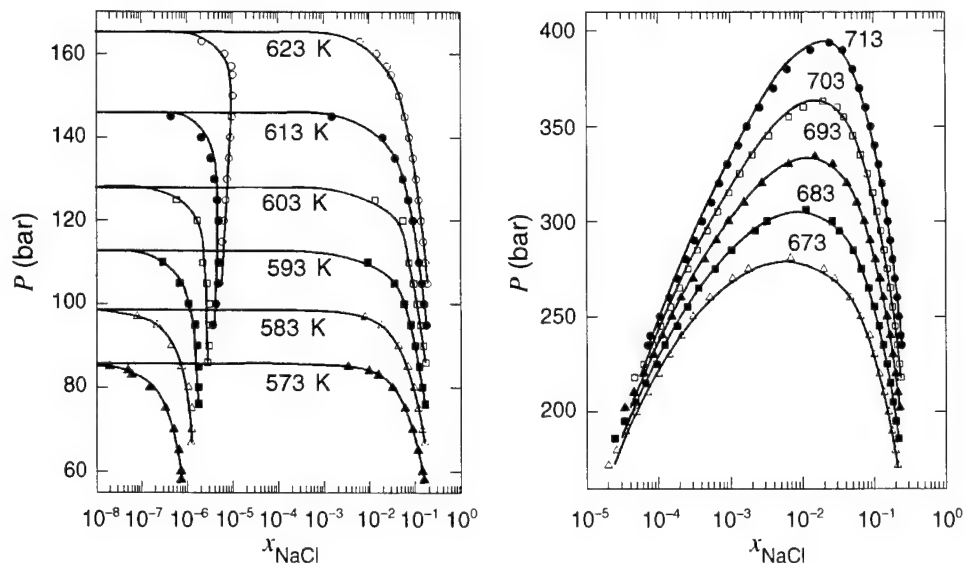


Figure 2. Densities of NaCl-H₂O mixture in vapor-liquid coexistence region and in one-phase liquid region (Anderko and Pitzer, 1993a).

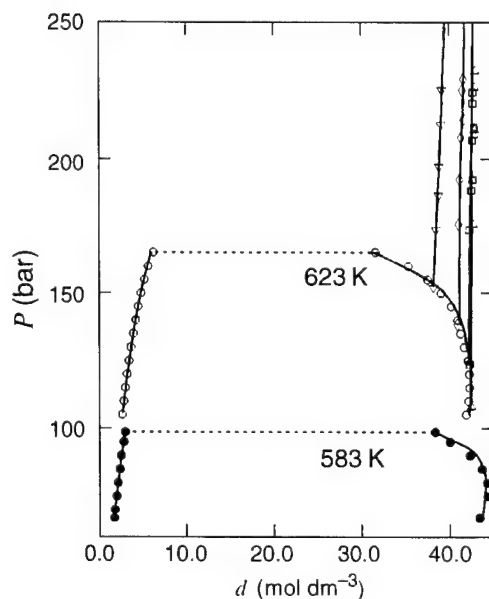


Figure 3. Solubility of solid NaCl in steam calculated from equation of state of Anderko and Pitzer (1993a).

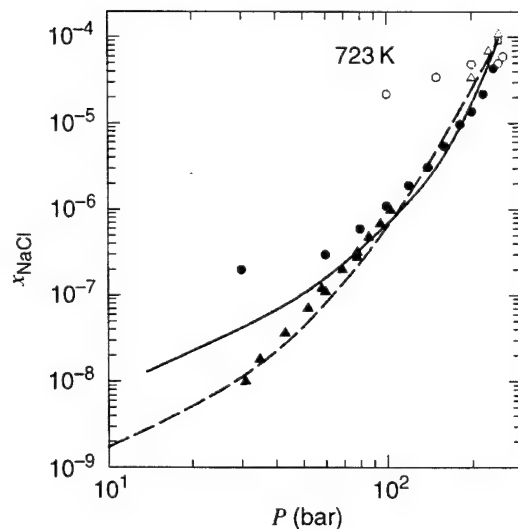
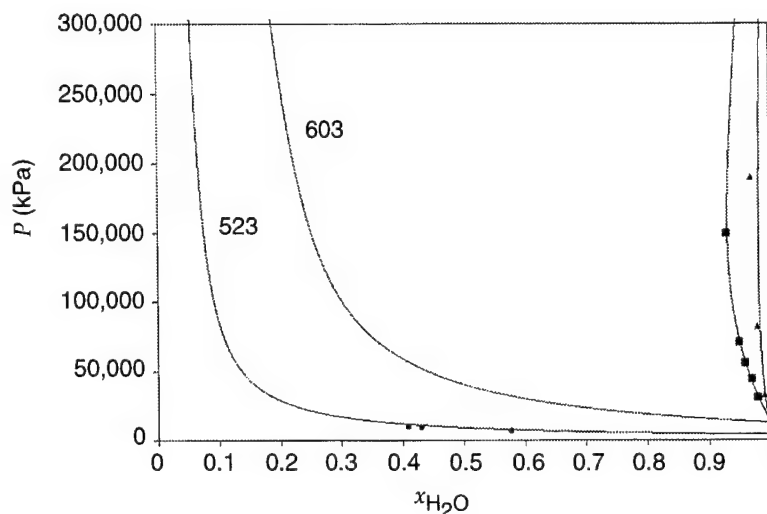


Figure 4. Calculated vapor-liquid equilibria calculated for O_2+H_2O system (Kosinski and Anderko, 1997).



Algorithm for Multiphase Equilibrium Computations

In addition to the accuracy of the equation of state, the robustness of the algorithm for solving phase equilibrium conditions is of utmost significance for practical applications. High-temperature salt solutions present a number of challenges for numerical algorithms because the systems have strongly asymmetric phase compositions. A useful algorithm must handle multiple solid phases and, in some cases, two liquid phases. Also, it has to be robust near the critical point. Kosinski and Anderko (1997) developed an algorithm that satisfies these conditions and tested it on selected systems.

Recent Work on Equations of State for High-Temperature Salt Systems

The concept of the reference state based on dipolar ion pairs has been widely accepted for modeling the behavior of high-temperature salt solutions and has been applied to several systems. In particular, Duan et al (1995) extended the equation of Anderko and Pitzer (1993a) to the ternary system $NaCl+CO_2+H_2O$. Thiery (1996) used the equation of state to construct computational modules for geologic applications. Economou et al (1995) coupled the dipolar reference state with another equation of state based on perturbation theory. Jiang and Pitzer (1996) extended the dipolar reference state to quadrupolar ion clusters and applied it to the $CaCl_2+H_2O$ system. Gallagher (1997) developed a similar equation of state for the $Na_2SO_4+H_2O$ system. Kosinski and Anderko (1997) applied the model to nonelectrolyte systems such as methanol + $H_2O+O_2+CO_2$.

Currently, work is in progress on extending the applicability of the equation of state to a larger group of components and to a wider temperature range. This work is being performed at OLI Systems under the sponsorship of the Army Research Office.

Unsolved Problems and Ideas for the Future

Although it has been demonstrated that equations of state of the type originally proposed by Anderko and Pitzer (1993a) can accurately reproduce the behavior of high-temperature salt systems, there are many unknowns, and much remains to be done. To transform the equation of state into a comprehensive tool for SCWO modeling and design, it would be necessary to—

1. Establish a database of available experimental data.
2. Develop parameters and validate the model for all relevant systems.
3. Develop a methodology for making predictions when few or no data are available.

Item 3 is especially important in view of the fact that very little experimental information is available for many systems of practical importance (e.g., fluorides, phosphates). It is possible that a corresponding-states-based method can be developed for salt solutions. For example, it has been demonstrated that a corresponding-states approach is viable for developing equations of state for pure ionic fluids (Anderko and Pitzer, 1992). Although an extension of this approach to solutions is not straightforward, it is worth investigating.

In the long term, it would be beneficial to investigate the issue of ionization in high-temperature water solutions. Although we can reproduce the phase equilibria and volumetric properties using the completely ion-paired reference state, a model that includes ionization/ion-pairing equilibria would be very useful for computing reaction equilibria in which ions participate. Also, it would be useful as a starting point for analyzing ion–metal surface interactions, which are essential for corrosion.

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Dielectric Constants of Aqueous Electrolyte Solutions at Elevated Temperatures

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A quantitative discussion and prediction of phase equilibria and fluid properties in aqueous electrolyte solutions will usually require the knowledge of the static dielectric constant (relative permittivity) ϵ of the solvent fluid or even that of the solution. The methods of prediction of the dielectric constant of polar fluids over a wide range of densities and temperatures, including the supercritical regime, are still in an early stage. Moreover, in contrast to a wealth of data at normal conditions, there is little knowledge on the effects of nonelectrolyte and electrolyte solutes upon the dielectric constant of water at elevated temperatures. With one exception [1], data for supercritical aqueous solutions are lacking. Moreover, in conducting electrolyte solutions, the conventional methods for determining the dielectric constant fail. Rather, one has to record frequency-dependent dielectric spectra at frequencies up to the gigahertz regime. The constant ϵ is then determined by zero-frequency extrapolation of the data. We at Bochum are currently developing an experimental technique for performing experiments at elevated temperatures and/or pressures with the aim of obtaining data in the supercritical regime as well. This contribution summarizes the current state of the art.

Figure 1 shows the temperature and density dependence of the static dielectric constant of pure water up to 1000 °C and a density of 1 g/cm³, derived from the measurements of Franck and coworkers [1,2] up to 550 °C and model calculations at higher temperatures [3,4]. Critically reviewed data are available [4]. The familiar high values of ϵ near 80 of liquid water occur in a narrow range of low temperatures and high densities. On the other hand, in an extended region of supercritical temperatures at high densities, ϵ is of the order of 10 to 25. Such values are typical for many polar solvents at ordinary conditions, so that one can learn about the state of the ions in such media from experiments on nonaqueous media. (At the critical point, $\epsilon \equiv 6$.)

Data for supercritical mixtures with simple nonpolar solutes, such as water + oxygen, are lacking. The only available data are those of Franck and coworkers on water + benzene to 400 °C and about 3 kbar [1]. I show in figure 2 an isotherm at 400 °C and 2 kbar as a function of the mole fraction x_1 of water. For comparison, I have measured data for aqueous solutions of dioxane at 100 °C. These data are also shown in figure 2, but are rescaled in such a way that for pure water the data points coincide.

Figure 1.
Approximate
representation of
static dielectric
constant ϵ as a
function of water at
temperatures up to
1000 °C and densities
up to 1 g/cm³ [5].

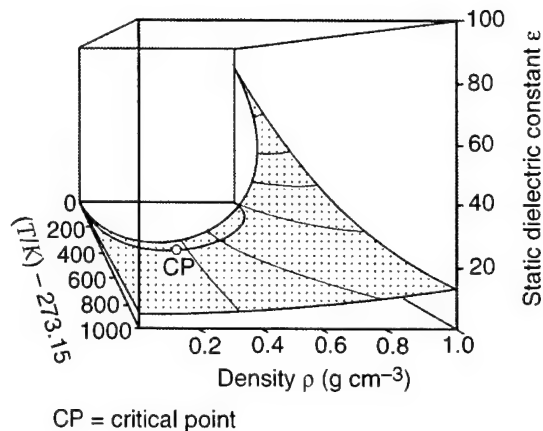
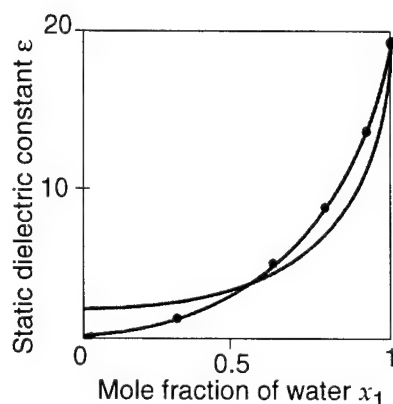


Figure 2. Dielectric
constant of mixtures
of water with
benzene at 400 °C
and 2 kbar (solid line)
and with dioxane
(line with circles)
at 100 °C. Data for
dioxane mixtures
have been rescaled by
factor 19.4/55.7 to
coincide for pure
water at 400 °C and
2 kbar.



In both cases, a drastic effect of the nonpolar solute on ϵ is found in the water-rich region. For example, for the mixture with benzene, the addition of only 10 mol % of benzene reduces ϵ from 20 to 10. In contrast, 50 mol % of water must be added to benzene for ϵ to increase from 2 to 4. Similar results are found with dioxane at much lower temperatures. Presumably, these results are typical for other nonpolar substances as well. A simple mixing rule of Looyenga [6] gives good quantitative predictions. As input data, this rule needs only the dielectric constant of the pure compounds and the densities of the mixtures. Thus, even with few data known, one could hope to construct a master curve that would allow at least semi-quantitative estimates.

Data for electrolytes at elevated temperatures are lacking. I have recently recorded dielectric spectra for aqueous solutions of LiCl at 95 °C (fig. 3), from which I have extrapolated the dielectric constant. At 25 °C, the addition of salts causes a rapid decrease of ϵ at low concentrations, which, however, seems to level off towards a value between 20 and 30 for the hypothetical molten salt. At 95 °C, effects are much smaller. I could meanwhile show with room-temperature molten salts that dielectric constants of molten salts are indeed of this order of magnitude. This has an immediate consequence for modeling the dielectric constant: If the dielectric constant of water is lower than 20 to 30, one expects an increase rather than decrease of ϵ from the addition of salt.

Figure 4 shows that this increase of ϵ with salt concentration is really observed in solvents of low ϵ . The example refers to a solution in dichloromethane ($\epsilon = 9.3$), where some organic salts with large ions are soluble. At concentrations of the order of 0.1 mol dm^{-3} , ϵ is about 1.5 times the value of the pure solvent. The spectra even allow one to separate the solvent and ion contributions to ϵ . It is seen that the increase of ϵ results from the ions only. The solvent contribution decreases slightly. Presumably, this only reflects the dilution of the solvent dipoles. Consequences for modeling are obvious, as many properties sensitively depend on ϵ .

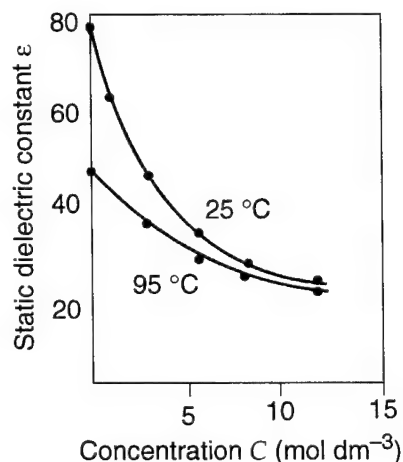


Figure 3. Dielectric constant of aqueous LiCl solutions as a function of molarity of salt.

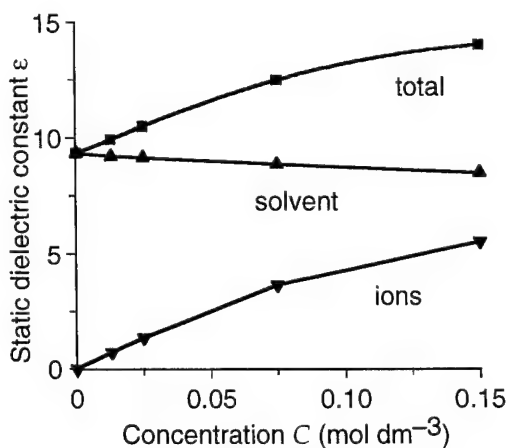


Figure 4. Concentration dependence of dielectric constant in solvents of low ϵ , with data for tetrabutylammonium iodide in dichloromethane at 25 °C used as an example.

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Phase Equilibria and Thermodynamics in High-Temperature Aqueous Systems

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Abstract

Although organic contaminants in aqueous solutions can be completely destroyed under appropriate supercritical water oxidation (SCWO) operating conditions, the potential application of this technology to a number of aqueous wastes is hindered by problems arising from inorganic chemistry (i.e., corrosion) and phase behavior, particularly deposition of solid phases on reactor system components. Investigations at ORNL of the fundamental equilibrium chemistry, chemical kinetics, and phase behavior of inorganic solutes in aqueous solutions have led to the development of experimental techniques and models for high-temperature solutions, and have contributed significantly to our understanding of inorganic aqueous chemistry under extreme conditions. Here I review those developments most directly related to an understanding of inorganic chemistry and phase behavior under SCWO conditions, with emphasis on general guidelines for operations based on specific experimental results.

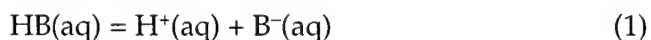
Introduction

Problems related to inorganic chemistry and phase behavior continue to limit confidence in the application of SCWO to wastes containing salts, oxides, and heteroatomic organic compounds (e.g., those containing sulfur, phosphorus, or halogens). A variety of potentially treatable substances in the U.S. Army inventory contain these materials, and guidelines for system operation that could avoid problems caused by these substances are important in determining the treatability of these materials. Quantitative models for the physical chemistry (reaction and solution thermodynamic properties) and phase equilibria in aqueous systems at high temperatures are of value in developing guidelines, particularly when the models demonstrate general physical trends that can be used in estimating values for systems where results are not available, or when the models can serve as surrogates (model-substance approach) for the system of interest. While some models have been developed strictly on theoretical grounds, a number of useful models have been based on a wide range of available experimental results; this discussion centers on the advances in model development and general understanding of the properties of aqueous systems at high temperatures that have accrued from detailed experimental investigations over wide ranges of temperature, pressure, and solution composition.

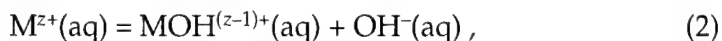
Models Based on Experimental Results

Homogeneous Reactions

Homogeneous reactions involving solutes in aqueous solutions have direct impact on important SCWO operating parameters, including the solution pH and the mobilization of species (primarily metals) by complexation. The generic acid–base ionization reaction



has been measured for a number of weak acids and bases at temperatures to 300 °C by the use of hydrogen-electrode concentration cells (HECCs) pioneered at ORNL (Mesmer et al, 1988). In specific cases the use of these cells can be extended to investigate the generalized hydrolysis of metal ions,



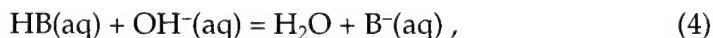
and the complexation of metal ions in solution by a variety of ligands (e.g., Palmer and Drummond, 1988; Palmer and Hyde, 1993; Wesolowski et al, 1998). Measurements of electrical conductance at high temperatures and pressures were used by Marshall and coworkers (e.g., Marshall and Mesmer, 1984) to develop a simple representation for ionization equilibria in aqueous solutions valid over wide ranges of temperature and solution density. In its simplest form, the equilibrium constant for a homogeneous reaction is given by

$$\log K = a + b/T + c \log \rho , \quad (3)$$

where

- K = equilibrium constant,
- T = temperature,
- ρ = density, and
- a, b, c are reaction constants.

With appropriate extension, equations of this form can be used to fit high-precision results from HECC studies as well as the original electrical-conductance measurements. Alternatively, rewriting reaction (1) using the ionization of water to give equal number and sign of charges on each side of the equation,



gives the “isocoulombic” form (Lindsay, 1980), for which the change in heat capacity of reaction is essentially zero. This is equivalent to noting that the value of the parameter c in equation (3) is nearly the same for the ionization of water as for a number of other weak-acid ionization reactions. Thus, for this important class of reactions, a wide variety of experimental results are available, and estimates of some reliability can be made for others if data are available near ambient conditions. Moreover, these correlations are useful for predicting and modeling liquid–vapor partitioning equilibria.

However, even with extensions of the model to represent the effects of ion association at high temperatures, the ion-interaction treatment will fail at conditions close to the critical point due to unphysical divergences in derivative properties (e.g., molar volumes), which arise from taking derivatives of the properties of water at constant pressure. Under such cases, equations that are based on solution volume as an independent variable, including the equation-of-state approach described in Anderko's contribution (pp 25–28), are more appropriate methods to represent the strongly nonideal properties of aqueous solutions.

Heterogeneous Equilibria

The thermodynamics of phase behavior are contained in measurements of heterogeneous equilibria. Three types of heterogeneous equilibria (liquid–vapor, liquid–liquid, and liquid–solid) may occur under SCWO conditions. Among these, the liquid–solid equilibrium is probably most important to process considerations, as dissolution of structural materials (corrosion) or precipitation of solid phases (deposition) can lead to system failure or plugging of components. It is not possible here to review the extensive literature, particularly from the power-plant steam generator community, on corrosion or on the deposition (or mobility) of solid salts. Even the knowledge of equilibrium thermodynamic properties for the formation of stable crystalline solids may be insufficient to represent phase behavior under SCWO operating conditions, because kinetics may allow the formation of metastable solid phases or eliminate deposition. No general model will be suitable for predicting this phase behavior under all operating conditions, and it seems clear that although broad guidelines for operation can be developed based on available information (e.g., phase diagrams of different types), closely targeted experimental studies will likely be required to demonstrate the suitability of a particular set of process conditions for use on a particular SCWO feed stream. A further complication arises from the surface charge existing on oxidized metal surfaces, which leads to adsorption of ions from solution (depending on pH, temperature, and the nature of the metal surface) and may also affect the rates of dissolution of the underlying metal (Wesolowski et al, nd).

A number of experimental methods are currently used in ORNL programs to study liquid–solid phase behavior at high temperatures. For sparingly soluble solid phases, particularly those with retrograde (decreasing with increasing temperature) solubility, gold-bag-lined rocking autoclave, HECC, and packed-column methods are being used at temperatures ranging to 400 °C and higher in some cases. The HECC studies are of particular interest for hydrolyzable metal ions or metal oxide phases, where the capability for direct *in situ* measurement of solution pH directly establishes the values of this critical variable in the experimental determinations (Brown et al, 1996; Wesolowski et al, 1998; Palmer et al, 1999). A primary challenge in measuring the solubility of relatively insoluble solids is the quantitative determination of the composition of the aqueous phase, with solute con-

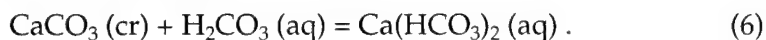
Excess Thermodynamic Properties

Accurate calculation of chemical equilibria in practical systems (i.e., those with finite solute concentrations) requires knowledge of the activity coefficients of the species involved. For example, the equilibrium constant for reaction (4) is

$$\log K = \log(m_B/m_{HB}m_{OH}) + \log a_w + \log(\gamma_B/\gamma_{OH}\gamma_{HB}) , \quad (5)$$

where the m are solute concentrations, and the activity coefficients γ may differ significantly from unity. Approximations and simplifications are appropriate for certain cases. In the example of equation (5), it is a reasonable first approximation to set $\gamma_B = \gamma_{OH}$, since each species has the same sign and magnitude of charge. Also, activity coefficients for uncharged species at low concentrations (e.g., undissociated acid HB) are often near unity at conditions away from the solvent critical point. Thus, neglecting all terms beyond the first on the right-hand side of equation (5) is a reasonable first approximation in this case.

Examples of nonnegligible activity coefficients often arise from the solubility product of solids in aqueous solutions. For the case of calcite dissolution in aqueous CO₂, the reaction is



In this case the equilibrium (solubility-product) constant is

$$\log K_{sp} = \log(m_{\text{Ca}}m_{\text{HCO}_3}^2/m_{\text{H}_2\text{CO}_3}) + \log(\gamma_{\text{Ca}}\gamma_{\text{HCO}_3}^2/\gamma_{\text{H}_2\text{CO}_3}) . \quad (7)$$

Values of γ_{Ca} and γ_{HCO_3} will be much different from unity under most SCWO operating conditions (high temperature, nonzero ionic strength). Calculations of equilibrium calcite solubilities given the value of K_{sp} could be in error by an order of magnitude or more if the activity coefficients are neglected. This potential error can be decreased if we use the extended Debye-Hückel limiting law or model substance approaches, but confidence in representing solubilities in such cases can best be gained through quantitative representation of experimental results based on an appropriate model for mixed-electrolyte solutions.

There is no fully satisfactory model for the excess thermodynamic properties of electrolyte solutions that spans the full range of SCWO operating conditions. The Pitzer ion-interaction model has been applied successfully to experimental results for simple electrolytes at temperatures through the solvent critical point (Busey et al, 1984; Simonson et al, 1987), but the model is data-intensive and not conducive to extrapolation in temperature or concentration. A significant set of experimental results on systems important to potential U.S. Army applications of SCWO is available from isopiestic studies carried out at ORNL to 250 °C by H. F. Holmes, including data on chlorides, sulfates, hydroxides, phosphates, and other compounds. In some cases, activity coefficients for simple salts have been estimated to higher temperatures through comparisons of activity coefficients with a model compound (e.g., NaCl) and extrapolating differences in $\ln \gamma$ to higher temperatures.

centrations as low as parts per trillion. Methods available for these analyses include inductively coupled plasma (ICP) and ICP/MS (mass spectrometry), ion chromatography, graphite-furnace atomic absorption, and recently developed capabilities for chemiluminescent detection of trace metal ions in solution (Xiao et al, nd). While such low solubilities are not generally of interest in determining conditions under which salt deposition would potentially plug operating SCWO reactors, even low solubilities of passivating oxide layers may lead to accelerated corrosion of reactor components.

Salts that can potentially plug SCWO reactor systems have characteristically moderate to high solubilities at near-ambient conditions; they may then show prograde (increasing) solubility with increasing temperature, followed by rapid precipitation as the density decreases strongly with increasing temperature above the critical temperature. Alternatively, salts such as sodium carbonate show a solubility maximum at some subcritical temperature above ambient temperature, with a reversal to retrograde solubility above the temperature of maximum solubility. It is of interest that not all salts of a particular type (e.g., alkali-metal carbonates) have similar solubility behavior. Potassium carbonate shows steadily increasing solubility from ambient temperature to $\sim 150^\circ\text{C}$; an inflection indicating a likely change in the number of waters of hydration of the solid is noted at this temperature, but solubility continues to increase, approaching $20\text{ mol} \equiv \text{kg}^{-1}$ at $\sim 250^\circ\text{C}$ (Moore et al, 1997). This is in marked contrast to the behavior of Na_2CO_3 , which shows a solubility maximum near 100°C with steadily decreasing solubility at high temperatures; its solubility is about $1.5\text{ mol} \equiv \text{kg}^{-1}$ at 250°C . Measurements such as those for K_2CO_3 , which one can obtain relatively simply using visually accessible cells, indicate that there may be significant advantages in SCWO processing of materials of interest to the U.S. Army through substitution of materials in preprocessing steps (e.g., caustic hydrolysis). Further experimental investigation of these possibilities is needed to confirm that such changes would simplify SCWO processing of certain materials. At ORNL, we have also developed a packed-bed, flow-through technique that permits *in situ* acidification of the solution at temperature as it exits the bed, thereby allowing measurements to be made of prograde solubilities of metal oxides and hydroxides.

Liquid-liquid and liquid-vapor phase separations in electrolyte solutions are important for "niche" conditions in SCWO systems. Acids and salts formed in the high-temperature reactor on oxidation of heteroatomic organic compounds will partition strongly to the first liquid condensate formed on cooling or quenching downstream from the reactor. An example of this behavior (for HCl) can be taken from the liquid-vapor phase distribution measurements reported by Simonson and Palmer (1993); similar data for other acids and salts of interest (including sulfuric and phosphoric acids and their ammonium salts) have been reported more recently (e.g., Palmer et al, 1998, 1999). A general guideline for avoiding this behavior in SCWO systems is that in cases where heat recovery is not necessary for economic operation, attemperation (quench) injection of water is the preferable cool-

ing method for the effluent stream, as that approach minimizes the possibility of formation of concentrated acidic salt solutions on initial formation of condensate.

Noncondensable gases (e.g., N_2 , O_2 , CO_2) present in SCWO feeds may also cause problems in the near-critical region owing to the effects of two-phase flow on fluid dynamics (heat and mass transfer); also, accurate knowledge of the density of mixed fluids at high temperatures gives greater confidence in calculating process variables such as retention time at various temperatures. High-precision measurements of the density and liquid-vapor phase envelopes of binary and ternary aqueous gas mixtures are currently being carried out at temperatures to 400 °C using a vibrating-tube densimeter (Seitz and Blencoe, nd). The enhanced precision of these measurements compared with earlier studies has prompted the development of new representations for the properties of mixtures based on the concept of "excess pressure." The available highly accurate equations of state for the pure fluids (e.g., H_2O+CO_2) are used to calculate "ideal" pressures of the mixed fluids from the measured molar volume at a given temperature, and the excess pressure is the difference between the measured and "ideal" pressures. The resulting surfaces for excess pressure as functions of molar volume and mixture composition are more regular (i.e., more nearly symmetric in x at constant T and V) than the excess volumes of the mixtures at constant pressure, and are therefore represented to high accuracy with simpler functional forms. Models being developed on this basis hold the promise of accurate representations, using a minimum number of well-behaved adjustable parameters, for mixture properties through the critical region of water.

Finally, it is important to note that given the difficulties in developing accurate parametric models for chemical equilibria and phase behavior in aqueous solutions that are valid over the full ranges of temperature, density, and composition of interest in SCWO processing, alternative representations based on a more complete understanding of interactions in solution at the molecular level are currently being actively pursued. These investigations, based on computer simulation by various techniques (e.g., molecular dynamics for homogeneous reactions; Gibbs ensemble Monte Carlo for phase equilibria), show promise in helping to develop a predictive capability that has proved elusive in describing the variation of behavior shown by aqueous systems over wide ranges of state variables. Recently, a rigorous formalism has been developed for separating the effects of solvation near solute species from the propagation of those effects through the (diverging) solvent compressibility near the critical point; this development may provide a starting point for the separation of phenomena common to all aqueous systems from those that are specific to a given solute (Chialvo et al, 1999). Such developments hold the promise of future development of more reliable guidelines for the operation of SCWO and other technologies at high temperatures with aqueous systems of arbitrary complexity.

Summary

While the development of general guidelines for SCWO operation is complicated by the diverse behavior of aqueous systems over wide ranges of temperature, density, and composition, numerous detailed experimental studies and models developed from those results can point out similarities between classes of solutes in solution, and can delineate areas where a closely focused experimental program could lead to significant advances in understanding of phase behavior and chemical equilibria. The extensive database for aqueous electrolyte thermodynamic properties available at temperatures to 250 °C provides a starting point for the wide-ranging representation of a number of important compounds. Completed and ongoing solubility measurements under extreme conditions are expanding the available data set and enhancing our understanding of general principles. New approaches to representing volumetric properties and phase behavior for aqueous mixtures (including noncondensable gases) are being developed based on experimental results of improved precision, coupled with highly accurate equations of state for pure substances. Finally, advances in computer power coupled with improved representations for intermolecular forces hold significant promise for further rapid developments in predictive capabilities.

Acknowledgements

This research was supported by the U.S. Department of Energy (Office of Basic Energy Sciences, Divisions of Chemical Sciences and Geosciences; Office of Environmental Management, Environmental Management Science Program; and Office of Energy Efficiency, Office of Geothermal Technologies) and by the Electric Power Research Institute under contract number DE-AC05-96OR22464 at Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corporation for the U.S. Department of Energy.

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Vapor-Liquid-Solid Phase Transitions in Aqueous Sodium Sulfate and Sodium Carbonate from Heat Capacity Measurements Near the First Critical Endpoint*

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Extended Abstract

Heat capacities at constant volume and composition have been measured for aqueous sodium sulfate for three compositions, 1 wt.%, 5 wt.%, and 10 wt.%, respectively, and along 19 isochores, from 250 kg·m⁻³ to 1073 kg·m⁻³, in the temperature range from 350 K to 670 K. The instrument is an Amirkhanov-type spherical adiabatic calorimeter, which is used in a ramping mode and is well documented in the English-language literature [1-4]. Temperature resolution is better than 0.01 K. Samples are prepared and filled by weight at ambient conditions, with uncertainty in density and composition less than 0.1%. Heat capacity values have an uncertainty of 1% to 2%, with uncertainties near critical lines increasing to 4% to 5%.

Sodium sulfate and sodium carbonate are Type 2 salts, for which the solid phase intrudes into the critical regime and cuts off the critical line [5].

In this presentation, we use the fact that the constant-volume heat capacity is a sensitive indicator of phase change. A jump, spike, or lambda-shaped change in the heat capacity is encountered when a phase change occurs. An increase in the background level indicates an additional phase appearing, and a decrease the disappearance of a phase.

* This paper is in preparation for *J. Chem. Eng. Data*.

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About 10 of the isochores show a downward jump when the vapor phase disappears from the cell. These jumps locate the boundary of the vapor-liquid region and were measured independently by Khaibullin and Novikov [6,7]. The agreement with these older data is well within the claimed uncertainty of the Khaibullin data.

Most isochores have been measured in the heating mode. In the range from 630 K to 650 K, many of them display two features: one peak when salt first precipitates and, on further heating, a second, lambda-shaped peak when the vapor or liquid phase disappears.

The first feature, the peak when the salt first precipitates, is particularly interesting. In the few cases where the isochore was also traversed in the cooling mode, only a step is seen approximately a degree below the peak in the heating mode. We interpret the peak in the heating mode as a hysteresis effect: suddenly, the system takes up heat as the solid forms from the superheated solution. In order to correct for hysteresis, we used an equal-area construction on all heating curves, thus locating the three-phase boundary temperature. We find the liquid composition by using the Khaibullin-Novikov liquid densities, while correcting for the steam phase by making use of pure-steam densities [8] at the given temperature and at the vapor pressure of the salt solution [6,7]. The new three-phase composition data are in good agreement with the data of Khaibullin and Novikov, and with several other literature sources.

The second feature, the lambda-shaped peak, indicates the disappearance of a phase (vapor or liquid) on heating. It is therefore not subject to hysteresis since no new phase is formed. The second peak always occurs close to critical conditions, where the isochoric heat capacity of a one-component fluid is known to have a lambda-shaped divergence. Although this lambda-shaped peak is usually suppressed in a binary mixture, here we have a special case, the presence of solid salt, which leaves the divergence intact. From the location of the second peak, we find the three-phase boundary temperature on either side of the critical end point, and since the salt concentration is very low for such points, we can calculate the amount of salt precipitated, as well as the density of the fluid phase. The present heat capacity data, as well as recent data for aqueous sodium carbonate, have sufficient resolution to distinguish, for the first time, the critical end-point temperatures in both aqueous sodium sulfate and aqueous sodium carbonate from the critical temperature of pure water.

Finally, on heating samples at high fill densities, the vapor phase may disappear before the salt precipitates. In that case, both density and composition of the liquid phase are known from the fill conditions, without the use of Khaibullin's data. Thus new densities are obtained for the vapor-saturated liquid density and composition in the absence of solid salt.

Salt deposition from aqueous sodium sulfate has recently been studied in a NIST/MIT collaborative effort [9]. Data on salt deposition from the vapor are part of a recent NIST correlation [10]

Two papers on the heat capacity work are in press [11,12].

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5. Invited Talks 3: Chemistry in High-Temperature Water

This last group of presentations discussed chemistry in high-temperature water, phase partitioning, and past technical advances. Ederer gave results of pyrolysis and oxidation reactions of simple organic compounds. Tester described hydrolysis, pyrolysis, thermolysis, and oxidation chemistry and salt-water-organic-gas phase partitioning in high-temperature water. Hong discussed a series of technical advances, represented by patents, that have signaled the progress of supercritical water oxidation; he focused on patents aimed at the need to handle precipitated solids and to avoid salt plugging.

Pyrolysis and Oxidation Reactions in SC Water

Hanns J. Ederer
Forschungszentrum Karlsruhe

Pyrolysis of t-butyl-benzene

A free radical mechanism was developed that describes the experimental data for for pyrolysis to t-butyl-benzene at 250 bar and a temperature range from 500 to 550 °C. Twenty-nine reaction products were measured. These were much more than expected, and the overall reaction rate was much slower than the initiation reaction known from literature as a normal-pressure gas-phase reaction-rate constant. The experimental and modeling experience may be summarized as follows:

1. There is no change or only minor changes in the thermodynamics between the hydrocarbon species, if a change from gas phase at 1 bar to SCW conditions is considered.
2. Therefore, the activation energies of the elementary reactions do not change with pressure.
3. The reaction rate constants of the elementary reactions with small molecules or reactions of small molecules remain the same or are faster compared with the same reaction at normal pressures. RRR or Troe theory may be used to adapt the parameters to the high pressures.
4. Large molecules react slower in SCW at the same temperature. The initial reaction's constant is more than a factor of 100 smaller, if one compares it to the gas phase data at 1 bar. The metathesis reactions also are slower by a factor of 10 to 100. The same slowing down of the pyrolysis rate has been found for the pyrolysis of ethyl-benzene. This can be explained by a diffusion control of the reaction or—which may be the same—by the cage effect.
5. If a traditional thermal decomposition reaction model is written down, one expects only four major products (methane, benzene, alpha-methyl-styrene, and isobutene). But in SCW the isomerization reactions become important, because many more products are found. (One of the main products (H_2) can be explained only if an isomerization of the primary radical is assumed.)
6. Substitution reactions are important in SCW conditions. More products are formed and can be explained only by substitution reactions. The cage effect is the main reason for this behavior. In ethylbenzene, the same pyrolysis is found (1 bar: styrene/toluene = 10/1; SCW: styrene/toluene = 1/10).

7. There is no influence of water as a reaction partner—experiments at the same temperature and pressure using N_2 give the same results.
8. These points may be generalized for hydrocarbons only, but not for substances containing heteroatoms or halogens.

Thermal Decomposition (Hydrolysis and Pyrolysis) of Glycerine

Many different substances have been found as main products of the thermal decomposition of glycerine at 450 bar and a temperature range from 620 to 750 K: acrolein, allyl-alcohol, propionaldehyde, acetaldehyde, H_2CO , $HCOOH$, CO , CO_2 , H_2 , small hydrocarbons, and higher condensation products. The global kinetics is about the order of one for glycerine at all temperatures, but the product distribution varies drastically with temperature, and the temperature dependence is non-Arrhenius. The mechanism that accounts for the behavior observed in the experiments consists of a free radical part and an ionic part. The ionic part is important (for flow and sensitivity analyses) at lower temperatures and the radical part at higher temperatures, and there is a region at about 700 K where both parts of the mechanism are involved substantially in the conversions of glycerine. The postulated mechanism may be summarized:

The oxygen-containing substances are thermodynamically stabilized by the SCW (compared with gas phase at 1 bar).

The radical part of the mechanism depends mainly on the temperature.

The ionic mechanism depends mainly on the ion product of water. (But of course the ion product at the same pressure of 450 bar depends on density and therefore on temperature.)

At high temperature (radical decomposition), there is a slowing down of the overall reaction rate with increasing pressure.

No data for the elementary reactions (even at the low-pressure gas phase) are available; the kinetic parameter was based on estimation rules only. The chemistry and the kinetic parameters of the energies of activation (EAs) are often pure assumptions (highly speculative), especially for the ionic part of the reaction mechanism.

There are oxidation (e.g., CO , CO_2) and reduction (e.g., H_2) products due to the chemistry of OH and H .

Experiments indicate that, for conversions up to 10%, only a relatively small mechanism (300 EAs) is needed for the description. For higher conversions at longer reaction times, a much larger mechanism (some thousands of EAs) containing also the decompositions of the products would be necessary.

SCWO

The following are conclusions drawn from experiments and a study involving the “complete C_1 mechanism” of Savage [1,2]:

The traditional combustion mechanism, with minor adaptations in the kinetics and the thermodynamics, describes SCWO reasonably well.

Important species are HO_2 and H_2O_2 .

There is a fast local equilibrium between $\text{H}_2 + \text{CO}$ and H_2CO , which causes the intermediate formation of CO and H_2 , even with an excess of O_2 .

For methanol with a less than stoichiometric amount of oxygen, there may be a total conversion of methanol to CO , H_2 , and CH_4 due to a free radical chain that is driven by H_2O_2 (formed in the first oxygen-rich part of the reaction).

The "complete C1"—or the "complete C2"—mechanism is not complete, because the chemistry of HCOOH has been neglected. Formic acid is not found in the usual combustion processes, but in SCWO experiments formic acid and its derivatives are found in larger amounts. Oxygen-containing (or heteroatom-containing) substances are stabilized in SCW.

Water is a reacting substance, but only to a very small extent.

Although water influences the combustion significantly, its influence is not great—by thermodynamic or maybe physical properties—if it is compared with oxidation in CO_2 at the same pressure and temperature.

For SCWO of substances with higher molecular weight, most of the oxidative chain reactions are within the C1 and C2 substances. The high molecular weight substance is primarily decomposed by pyrolysis (retardation?) or hydrolysis to C1 and C2 species.

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1. Savage, P. E., N. Stylski, J. Yu, and E. E. Brock (1998). "Kinetics and mechanism of methane oxidation in supercritical water," *J. Supercrit. Fluids* **12**, 141–154.
2. Brock, E. E., P. E. Savage, and J. R. Barker (1998). "A reduced mechanism for methanol oxidation in supercritical water," *Chem. Eng. Sci.* **53**, 857–867.

Chemical and Phase Reactions in Supercritical Water

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Two main areas are covered in this presentation: (1) hydrolysis, pyrolysis, thermolysis, and oxidation chemistry, and (2) salt-water-organic-gas phase partitioning in both hydrothermal and supercritical environments from temperatures of 100 to 650 °C and pressures up to 1000 bar. During the oxygen-free preheating phase of injection of organic feeds into supercritical water oxidation (SCWO) reactors, hydrolysis, pyrolysis, and thermolysis reaction pathways can be important and, with sufficiently fast kinetics, can result in char formation (pyrolysis) or acid production from the hydrolysis of heteroatom-containing organics (e.g., HCl from H-C-Cl compounds). Oxidation in supercritical water proceeds rapidly with sufficient oxygen and temperatures in excess of 500 °C to produce lower molecular weight H-C-O products. Eventually, after residence times of about 1 minute, full mineralization occurs to CO₂, H₂O, molecular N₂, and inorganic acids associated with the heteroatoms (Cl, S, P, F). A key area many research groups have focused on is characterizing the rates and mechanisms of hydrolysis and oxidation reactions of model compounds under well-defined reaction conditions of T , P , ρ , x_i , and residence time (Tester et al, 1993, 1998; Savage et al, 1995, 1999).

In the second area, the research focus has been on experimental characterization of phase boundaries and compositions in binary (single salt-water) and ternary (two salt-water) systems (e.g., Armellini and Tester, 1993; DiPippo et al, 1999) and on modeling of salt-water systems in general (Cui and Harris, 1995a,b; Reagan et al, 1999; Tester et al, 1998).

Chemical reaction studies typically produce isothermal kinetic data under a range of conditions of pressure/density, organic/oxygen ratio (fuel equivalence), residence time, and feed concentration in several different reactor configurations, including plug flow tubular, continuously stirred tank reactor (CSTR), and batch systems. Global rate expressions, including reaction orders and activation energies, are available for a number of model compounds, including H₂, CO, CH₃OH, CH₃OOH, CH₂Cl₂, C₆H₆, C₆H₅OH, TDG (thiodiglycol, (CH₃)₂S-(OH)₂), glucose, and MTBE (methyl tert-butyl ether) (Tester et al, 1993a,b; Holgate et al, 1995; Meyer et al, 1995; Lachance, 1995; Lachance et al, 1999; Marrone et al, 1998a,b; Salvatierra et al, nd). Except for TDG, MTBE, and CH₂Cl₂, the other compounds do not hydrolyze rapidly at temperatures up to 550 °C. Oxidation is rapid above 500 °C and complete for all compounds after 60 s exposure at 600 °C. TDG and CH₂Cl₂ react at subcritical temperatures with water to produce H₂SO₄ and HCl, respectively, and partially oxidized H-C compounds. These inorganic acids can be neutralized easily with NaOH to produce Na₂SO₄ and NaCl salts.

Successful quantitative modeling of hydrolysis has been achieved by modification of Kirkwood's treatment of dielectric effects on transition state structures to explain the significant decrease in hydrolysis rates above the critical point of water (Marrone et al, 1998, 1999). Oxidative pathways in the supercritical region have been analyzed via free-radical elementary reaction modeling based on combustion theory and modified for high-pressure/high-density operation by extended RRKM corrections. In addition, molecular, mesoscale, and global modeling efforts are under way to correlate and evaluate important trends observed experimentally. For example, various researchers (at MIT, NIST, ORNL, and elsewhere) are quantifying the PTx_i behavior of the NaCl–Na₂SO₄–H₂O binary and ternary systems using the Anderko-Pitzer model and other theoretically based equations of state (see papers presented by Anderko and Simonson from this workshop for further details). In separate studies at MIT and ORNL, molecular simulations are being used to shed light on important phenomena in hydrothermal and supercritical salt solutions, such as local solvation and solution structure, hydrogen bonding, ion pairing, solid phase nucleation, phase coexistence, and spinodal decomposition (Reagan et al, 1999).

Some effort has also been placed on characterizing nucleation rates and the solid salt morphology that appears during precipitation from highly supersaturated NaCl, Na₂SO₄, and Na₃PO₄ brines (Armellini and Tester, 1991; Armellini, Hong, and Tester, 1994; DiPippo, 1997; DiPippo, Sako, and Tester, 1999; Hong et al, 1995). These studies have shown that the presence of liquid phases in Type I synthesis, in coexistence with lower density supercritical fluid or vapor phases, can greatly influence solid particle nucleation and morphology in the case of NaCl deposition. In contrast, Type II salts, such as Na₂SO₄ and Na₃PO₄/Na₂HPO₄, show rapid homogeneous-type nucleation of microparticles that agglomerate as precipitation proceeds. Dynamic light scattering methods have been used to characterize particle sizes during salt precipitation.

In summary, chemical reactions can have a direct effect on the appearance of secondary phases (1) because the possible different products of both oxidation (CO₂, CO, ...) and hydrolysis (HCl, H₂SO₄, ...) pathways determine composition (x_i) and (2) because the heat of reaction can influence fluid temperature, thereby altering PTx_i behavior. Under favorable thermodynamic conditions, phase separation reactions can occur very rapidly to nucleate both liquid and solid phases in the presence of a low-density supercritical vapor phase. Although coexistence boundaries are known for several common systems, like NaCl–Na₂SO₄–H₂O, they are largely uncharacterized in the hydrothermal and supercritical regions for most other salts, especially fluorides and phosphates. Little experimental data are available on the rates of phase nucleation and growth in the supercritical region for all salts.

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Reactor Engineering and Phase Separations in SCWO

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The need to handle precipitated solids within a supercritical water oxidation (SCWO) reactor is frequently the overriding factor in its design. The earliest work on reactor designs was carried out at Modar, Inc., starting in 1981. Since that time, numerous U.S. patents have been issued that deal with the need for handling solids within the reactor. A survey of such patents has been carried out as of June 1999, the results of which are presented in table 1.

Table 1. Patents as of June 1999.

Pat. No.	Method	Date	Author	Assignee
4,543,190	Inclined settler	24/09/85	Modell	Modar
4,822,497	Reversing flow vessel with brine pool and filtration	18/04/89	Hong et al	Modar
5,100,560	Cylindrical scraper	31/03/92	Huang et al	ABB Lummus Crest
5,200,093	Reactor exit quenching	06/04/93	Barner et al	ABB Lummus Crest
5,250,193	Subcritical temperature	05/10/93	Sawicki et al	Air Products and Chemicals
5,252,224	Velocity pigging ^a	12/10/93	Modell et al	Modec
5,384,051	Transpiring wall	24/01/95	McGuinness	Inventor
5,387,398	Transpiring wall	07/02/95	Mueggenburg et al	Aerojet General
5,421,998	Cross-flow filtration	06/06/95	Li et al	University of Texas
5,425,883	Centrifugal reactor	20/06/95	Reid et al	Inventors
5,427,764	Vortex, high pressure operation	27/06/95	Barber	RPC Waste Management
5,437,798	Washed wall	01/08/95	LaRoche et al	Sulzer Chemtech
5,461,648	Helical scraper	24/10/95	Naufflett et al	U.S. Government
5,501,799	Alternating reactors	26/03/96	Bond et al	Abitibi-Price
5,543,057	Inert solids addition	06/08/96	Whiting et al	Abitibi-Price
5,560,823	Reversing flow pipe	01/10/96	Whiting et al	Abitibi-Price
5,571,423	Transpiring wall	05/11/96	Daman	Foster Wheeler
5,620,606	Inert solids addition	15/04/97	McBrayer, Jr., et al	RPC Waste Management
5,755,974	Eutectic formation	26/05/98	McBrayer, Jr., et al	RPC Waste Management
5,890,531	Periodic pigging ^a of pipe reactor	06/04/99	Gairns et al.	Noram

^aPigging is a technique in which a cleaning device is allowed to travel through a pipeline under the propelling action of the flowing fluid. The "pig," which may be a billet of material with brushes, travels from one end of the pipe to the other, brushing or scraping off solid deposits from the pipe inner diameter. The pig is removed from the line (or at least from the active flow path) at a downstream point.

6. Reports of the Focus Groups

6.1 Focus Group A

6.1.1 Members

Dr. Glenn T. Hong, General Atomics, U.S.
Dr. J. M. Simonson, Oak Ridge National Laboratory, U.S.
Prof. Jefferson F. Tester, Massachusetts Institute of Technology, U.S.
Prof. Hermann Weingärtner, Ruhr-Universität Bochum, Germany
Dr. Nikolaos Boukis, Research Center Karlsruhe, Germany
Dr. Cor J. Peters, Delft University of Technology, The Netherlands
(rapporteur)

6.1.2 Introduction

Focus Group Alpha was requested to come up with guidelines/rules of thumb to provide insight into the occurrence of phase separations at the various stages of a supercritical water oxidation (SCWO) process for the destruction of a variety of military wastes. For that purpose, Focus Group Alpha considered a compilation of possible wastes (see table 1, p 11), prepared by Glenn Hong, Jeff Tester, Steve Buelow, and Bob Shaw, which was made available before the meeting. Based on the various introductory presentations and individual specific expertise of the participants, Focus Group Alpha realized the following:

- We are dealing with complex mixtures of molecules that may form multiple phases (fluid and solids) at any stage of the SCWO process.
- Directional forces between the various species in the mixture play an important role with respect to the (multi-)phase behavior to be expected.
- Because in the open literature the availability of experimental information on model systems of interest for the real process is extremely limited, this information will not be representative enough to provide even qualitative insight into the phase behavior that may occur in real mixtures. Further, although some experimental information is available in the Russian literature, this information is often very hard to evaluate.
- Predictive (semi-)empirical thermodynamic models and models based also on statistical mechanical considerations are not yet developed to such a level that they can be used for phase equilibrium predictions of the mixtures of interest for SCWO.
- The properties of the feed are not always known.

6.1.3 Aspects Taken into Account

Focus Group Alpha would like to emphasize that substantial basic knowledge is urgently needed to support optimum designs of SCWO processes; research in this topical area is highly recommended. From the meeting it also became apparent, however, that the time required for even minimal basic research in this area is excessive in the light of the urgency of the need for facilities to process and destroy military waste streams. Consequently, at the beginning of their discussions, this Focus Group decided to follow an “engineering approach”; that is, we accept that a number of practical issues cannot be sufficiently supported by basic knowledge. According to this approach, the following aspects were taken into account:

- Safety of operation.
- Corrosivity at the various stages of the process.
- Plugging due to precipitation of solids.
- Erosion in the facilities due to the presence of precipitated solid inorganic products in the process streams.
- Multiphase behavior (solids, liquid, and vapor), which was considered to be unavoidable in all stages of the process.
- The fact that the SCWO process does not necessarily have to be energetically self-maintaining.
- The treatment of all kinds of waste during the three main stages of the process: heating up (temperatures up to 375 °C), reaction (375 °C < t < 650 °C), and cooling down (temperatures below 375 °C).

6.1.4 General Recommendations and Suggestions

This section offers a number of general recommendations on operating an SCWO process for the destruction of military waste streams.

In general, it is preferable to operate the process at low feed concentrations. This has the advantage that in the heatup stage of the process, undesired reactions can generally be avoided. For instance, the formation of nitrates in excessively high concentrations may cause self-oxidation and possibly may lead to an uncontrollable runaway effect. Moreover, undesired reactions also may generate highly corrosive reaction products at places in the facility that are not adequately resistant to or protected against corrosion.

Another advantage of low concentrations is that since we have to assume that solid material will almost always be present in the process streams at every stage, solid particles in a diluted regime are less likely to form aggregates that may plug the connecting lines.

In order to avoid reactions occurring outside the reactor itself, in general cold injection of the feed is recommended.

It is recommended that pure oxygen be directly injected into the reactor as the oxidant. If, for instance, air were used, there would be too high a gas volume in the process stream with inert nitrogen as the major constituent. An additional problem with the presence of too much inert gas in the process stream is that the nitrogen may act as an antisolvent, so that the solubility of dissolved salts will decrease and salts will precipitate.

The presence of dissolved salts in the process stream may reduce the solubility of the oxygen in the fluid phase, which has important consequences for the nature of the oxidation reaction and for reaction time. Another potential problem is that oxygen could be trapped in precipitated salts.

After it leaves the reactor, the process stream should be quenched to 250 °C. This has the advantage that certain salts will redissolve.

Sometimes it may be better to neutralize the acidic product stream with KOH rather than with NaOH, because KCl, for instance, has a higher solubility than NaCl. However, a disadvantage of this choice is that KCl is much more corrosive than NaCl.

The members of Focus Group Alpha agreed that excessive effort should not be applied to reducing the number of phases in the process stream. The presence of multiple solid phases, a liquid phase, and a vapor phase has to be accepted as given. Manipulating such process streams is a very well-known engineering problem and can be handled in practice.

6.1.5 Specific Recommendations for Various Waste Streams

Specific recommendations are provided below on treating the various waste streams, as summarized in the table 1 of Hong's paper (p 11).

Explosives and propellants

For safety reasons, the feed needs to be hydrolyzed at low pressure and at a temperature not exceeding 100 °C. In order to avoid corrosion in later stages of the process, an excess of NaOH should be avoided. The latter especially is important for waste stream A2, since it already contains NaOH. The hydrolysis will lead to the formation of nitrates and acetates, with the result that in the preheating phase of the process (to temperatures as high as 300 °C), self-oxidation may occur. In order to prevent a runaway effect during this stage of the process, it is recommended to operate in a highly diluted regime.

Halogenated organics

In category B1, surfactants containing S and P should be avoided, since phosphates and sulfates will be formed. Since phosphates have an extremely low solubility, they will precipitate easily. On the other hand, Na_2CO_3 may cause the formation of sticky salts. In order to avoid sticky salts, KOH could be considered as a neutralizing agent, which will lead to the formation of K_2CO_3 . However, a disadvantage of this approach is that we lack the phase

diagram of $\text{H}_2\text{O}+\text{K}_2\text{CO}_3$. Another suggestion is that it might be necessary to apply defoaming agents in the treatment of substances belonging to category B1.

With respect to categories B2 and B3, Focus Group Alpha would like to stress that processing in a diluted regime is a prerequisite, and that fuel may even be added in this case. Furthermore, pre-neutralization with NaOH is recommended, along with cold injection into the reactor. Also, KOH can be used as a neutralizing agent. The advantage is that KCl has a much higher solubility than NaCl and, consequently, there will be less risk for plugging. On the other hand, the KCl brine will be more corrosive. For corrosive brines, a more resistant material, such as alumina, should be considered as the reactor material.

Chemical weapons

For chemical weapon wastes, hydrolysis of the feed is necessary. The main problem related to this category is that in almost all cases we are dealing with precipitation of phosphates like NaH_2PO_4 and Na_2HPO_4 . Although quantitative information does not exist, it is estimated that the solubilities of these phosphates will be extremely low. Also, we require data on the system $\text{H}_2\text{O}+\text{NaF}$. Bearing in mind that potassium salts show higher corrosivity, note that the solubility of KF is significantly higher than that of NaF, which also has its advantages during processing. Especially for this category of wastes, processing in a dilute regime is strongly recommended, which will keep the particle density low. Cold injection of the hydrolyzed feed is not necessary.

Organic wastes

In general, for organic wastes, cold injection of the feed into the reactor is possible. KOH is suggested as a neutralizing agent. Somewhere downstream, a quench stream should be incorporated in the flow, in order to redissolve salts.

For subcategory D3, Focus Group Alpha does not have clear recommendations because of the presence of inorganic material in the feed.

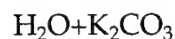
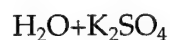
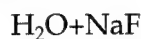
6.1.6 Recommended Research

From the recommendations above, it should be apparent that from a phase theoretical point of view we are dealing with extremely complex systems; many different components will be present in the mixtures, many of which show strong mutual molecular and/or ionic interactions. Without any doubt, this complexity will lead to complex multiphase behavior. Because of the complexity of the mixtures, there are neither experimental data on representative systems nor predictive thermodynamic models available that will offer sufficient insight for an optimum process design.

Therefore, it is strongly recommended that additional research be pursued on carefully selected systems to fill the most important gaps in basic knowledge. Some highly recommended research is given below.

Experiments

Experimental investigation is recommended into the high-temperature/high-pressure phase behavior of the following systems:



In the pressure and temperature regime of the cooldown stage of the process, there is no information available on how dissolved gases like CO_2 , N_2 , and O_2 may influence the solubility of salts in the fluid phase. It is expected that these gases act as antisolvents with a consequent decrease in the solubility of the salts; i.e., an enhanced precipitation will occur.

Modeling

As became apparent at the workshop, currently available models still cannot treat real systems as they are met in practice. In particular, the modeling of the complex ionic solutions is extremely difficult. As long as the ions can be considered as ion pairs, there are possibilities for predictive modeling (see the contribution of Anderko, p 25). However, at various stages of the process, this condition is not fulfilled, and currently available models will fail. Therefore, better predictive models should be developed.

6.2 Focus Group Ω

6.2.1 Participants

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Dr. Hanns Ederer, Research Center Karlsruhe, Germany
Prof. E. Ulrich Franck, Emeritus, Universität Karlsruhe, Germany
Dr. Johanna Levelt Sengers, Emeritus, National Institute of Standards and Technology, U.S. (rapporteur)
Dr. Helmut Schmieder, Research Center Karlsruhe, Germany
Dr. Robert Shaw, Army Research Office, U.S.

6.2.2 Phase Behavior (First Part)

Rule of Thumb 1

All gases/organics will be completely miscible with water (or destroyed) above 400 °C and at pressures above 100 bar and up to at least 1 kb.

Note: This statement assumes that equilibrium has been reached; it is not necessarily true for short residence times or in the absence of stirring or mixing.

Rule of Thumb 2

Type 1 salts (for which the solid does not intersect the vapor–liquid critical line) will show vapor–liquid phase separation beginning in a region that is roughly the extension of the vapor pressure of pure water in the P – T phase diagram.

There are sufficient data for the sodium and potassium halides and hydroxides to delineate this region in P – T , as well as in T – x and P – x space, up to 700 °C and 1 kb.

The location of the S – L – V line in the Type 1 salts is of major concern, because its maximum may be located well above the critical pressure of water. No general rule is available.

Rule of Thumb 3

Franck hypothesis: Above 400 °C, and at densities below 0.5 kg dm^{−3}, no divalent ions exist. They are partially or fully associated.

Rule of Thumb 4

Type 2 salts (for which the solid interrupts the vapor–liquid critical line), the solubility decreases with temperature (the temperature–liquid composition three-phase curve moves to lower compositions at increasing temperature). Salts in this class have at least one divalent ion, but salts with one divalent ion are not necessarily Type 2. Type 2 salts will always produce solids under SCW conditions.

Examples are aqueous Na_2CO_3 , Na_2SO_4 , and K_2SO_4 . Some phosphates have more complex behavior, where an L - L - V critical line persists near the water critical point.

Rule of Thumb 5

Binary fluid phase diagrams of interest to SCWO applications are mostly Type I (continuous critical line) and Type III (critical line interrupted by L - L - V three-phase line).

Examples of Type I are aqueous alkali halides and alkali hydroxides; aqueous NH_3 ; and aqueous HCl . Examples of Type III are hydrogen, air constituents, noble gases, and organics in water. The hydrogen system may be of importance and concern: the presence of hydrogen may lead to embrittlement. Electrolysis of water may be a good source of oxygen, but does also produce hydrogen. For the system NH_3 - H_2O , there has been much recent experimental work, as well as a new NIST database and correlation in connection with the proposed Khalina cycle.

Rule of Thumb 6

Knowledge of the initial slopes of the critical line in P - T , P - x , and T - x space yields the useful Krichevskii parameter, which characterizes solute-mixture behavior near the solvent critical point.

6.2.3 Research Needed to Characterize Phase Behavior

Nucleation, including rates

The following data are needed:

- phase boundaries for the solid and
- superheating data.

Experiments should focus on practical needs:

- Highest priority studies are sodium and calcium sulfates and phosphates.
- Experiments should be performed in flows.
- Nucleation rates and salt morphology should be determined.
- Means of dissolving or dispersing solids (e.g., ultrasound) should be explored.
- Means to avoid, suppress, or control nucleation should be explored.
- The effects of high pressure (which may limit upper temperature range) should be investigated.
- Cosolvents should be investigated.
- Fluidizing solids by suspension/emulsion should be investigated.

- Use of emulsions to disperse solids and control oxygen admission should be explored. An emulsion was observed by E. U. Franck and coworkers in aqueous methane at high pressures and temperatures. K. Johnston (U. Texas) has investigated emulsifiers in SCW.

Transport properties

Transport properties are needed for the calculation of design parameters such as heat transfer coefficients. Here, the following simple rules of thumb can be formulated:

- The use of pure water properties as a function of temperature and pressure will lead to large errors when electrolytes or gases are present in supercritical water systems.
- For water + gas systems, transport properties can be roughly estimated based on available correlations. However, no models are available for electrolyte-containing supercritical water systems. Also, there are virtually no experimental data for such systems.

Two methods for obtaining design parameters are available: (1) measurement of transport properties, which could then be used in computing design parameters, or (2) empirical determination of design parameters.

Empirical determination was judged more practical because we know very little about transport properties in high-temperature salt solutions. Therefore, acquisition of fundamental transport property data would be a daunting task. Besides, it is advisable to focus the limited experimental resources that are available on phase equilibrium measurements, because they are more critical than transport properties.

Ternary and multicomponent systems

The importance of phase equilibria in multicomponent systems has been emphasized. It has been recognized that simple rules of thumb are difficult if not impossible to formulate here. Instead, a research program is needed to establish models that predict the behavior of multicomponent systems.

An old rule of thumb says that the binary solution $\text{NaCl}+\text{H}_2\text{O}$ can be used as a pseudofluid for predicting the properties of multicomponent systems. However, this rule of thumb is too inaccurate to be useful. Thus, there is no substitute for fundamental modeling.

There is a need for—

- Experimental determination of the properties of model ternary systems. Currently, data are available only for $\text{NaCl}+\text{CO}_2+\text{H}_2\text{O}$, $\text{NaCl}+\text{CH}_4+\text{H}_2\text{O}$, and $\text{LiBr}+\text{CH}_3\text{OH}+\text{H}_2\text{O}$.
- Development of equations of state for systems containing salts, water, and gases. Some concern was voiced regarding the estimation of parameters for such equations. The parameters would have to be

determined for the constituent salt–water and water–gas binaries. Then, they would have to be estimated for the salt–gas binaries because no data are available for such subsystems. However, there is optimism that this problem can be overcome and satisfactory equations can be developed.

Database of phase equilibria in salt–water systems

A database of phase equilibria in high-temperature salt–water systems is needed to support the advancement of both experimental and theoretical work. The currently available experimental data are scattered in the literature, they are sometimes published only in difficult-to-obtain journals without an English translation, and they lack any critical evaluation. Thus, a comprehensive database in electronic form would be of immense value. The group discussed how to approach the problem of creating the database.

What to collect?

Here, a simple rule of thumb would be to collect relevant experimental data for temperatures above 200 °C. No upper limit is necessary, because very few experimental data sets go to temperatures that are above the practical limit of SCWO processes.

How to do it?

A computerized database would be vastly superior to a printed collection. Such a database could be continually updated and corrected.

Who could do it?

The organization that creates the database should be in a position to make a long-term commitment to maintain and update it. Also, it should have technical expertise in high-temperature salt systems and should be competent in the area of software development. These criteria suggest three possible candidates: NIST, Oak Ridge National Laboratory, and OLI Systems. In addition to the prime developer, a steering committee should be established from the workshop participants. Dr. Valyashko of the Russian Academy of Sciences would be asked to help with the collection and interpretation of some Russian data. Also, we encourage input from the geological community (American Geophysical Union) and materials research community.

Reactor Safety

Flames were briefly mentioned as a safety concern. It appears that they can be avoided by appropriate design of mixing devices. Thus, this problem does not seem to call for thermodynamic investigations.

Hydrogen embrittlement is another safety concern. It is more common in oxygen-free systems, where accumulation of hydrogen is possible. A rule of thumb has been formulated that hydrogen embrittlement can be avoided by the use of iron-free alloys.

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